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FOLIAGE AND BARK
AS MODIFIERS FOR PLYWOOD UREA-FORMALDEHYDE RESINS



by

DANILO ADOLFO ROSALES URBANO

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c Danilo Adolfo Rosales Urbano

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Department of Forestry

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date October 14, 1980.

ABSTRACT

This work follows successful research by staff members at Forintek Canada Corp. in modifying and extending phenol-formaldehyde (PF) plywood resins with powdered tree foliages and barks.

In the present study, two urea-formaldehyde (UF) resins, one commercial and one laboratory synthesized, were modified at 15, 30 and 45% addition levels with finely ground white spruce [Picea glauca (Moench.) Voss] foliage or western hemlock [Tsuga heterophylla (Raf.) Sarg.] bark. Two five-ply Douglas-fir [Pseudotsuga mensiezii (Mirb.) Franco] test plywood panels (38 x 38 cm) were made at 32kg/100 m² double glueline spread level, six and ten min pressing time at 149°C.

The commercial and laboratory synthesized wheat flour extended UF resins were used as controls. Shear strengths and wood failure percentages were recorded for sets of test specimens after conditioning at 22°C and EMC of about 6% (Dry test), one vacuum pressure cycle, five vacuum pressure cycles and boiling cycle.

Most formulations with the commercial UF resin containing foliage or bark yielded good bond quality (wood failure and shear strength) similar to the control when tested dry and after one vacuum pressure cycle. Following

multi-cycle testing, one formulation containing foliage gave similar wood failure percentage to the control. Two formulations containing bark improved glue bond durability yielding 3 to 12% higher wood failure than the control. Results with the laboratory resin were not as good, showing bond quality lower than with the commercial UF formulation. No formulation survived boiling treatment implying that no modification among those used improved UF resin durability under conditions of high moisture and temperature.

Both UF resins were successfully extended by various foliage and bark additions. It was found that both materials can be used as partial substitutes for the conventional extender wheat flour up to the 40% level.

This information may be of use to some developing countries that import wheat to flour-extended UF resins used to bond interior grade plywoods. Such countries could benefit by making use of local tree foliages or barks.

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1.0 INTRODUCTION

Urea-formaldehyde (UF) is the typical resin used in hardwood plywood manufacture. The cured glue produces good, water resistant bonds but is restricted to interior use because of susceptibility to hydrolysis at higher temperatures (about 60°C) in the presence of moisture (Troughton, 1968). Recent concern on price and availability of petroleum, the raw material for exterior grade phenolic resins, provides incentive for developing new non-petroleum based resins or for improving durability of existing interior quality adhesives.

Many studies (Blomquist and Olson, 1964; Gillepsie et al., 1964; Steiner, 1973; Steiner and Chow, 1974) have indicated that UF modification with synthetic or natural materials improves durability. For example, UF modifications with melamine, polyvinyl acetate, furfuryl alcohol, additional urea and other materials have improved UF bond durability.

In the last few years interest has focussed on using foliage and bark as extenders or substitutes for resin itself, especially with phenol-formaldehyde (PF). Research conducted at Forintek Canada Corp. has indicated that both materials have good adhesive properties (Steiner and Chow, 1975; Chow, 1977; Chow, Steiner and Rozon, 1979).

Wheat flour is the typical extender in UF and PF mixes. In UF formulations, the extender comprises about 40% of the mix total solids content. The amount of wheat flour used for plywood manufacture is enormous. In North America the total amount employed for this purpose is more than 45 thousand metric tons per year, in Far East countries more than 200 thousand metric tons per year are used (Barton et al., 1978). In Peru, the plywood industry uses only UF resin and the consumption of wheat flour is more than one thousand metric tons per year (Rosales, 1980).

The price of wheat flour has tripled in recent years to about 20 to 25 Cdn. cents per kg and supply for this purpose is in competition with food needs. This is aggravated in developing countries where the import cost of wheat flour is a great burden. The importance of replacing wheat flour by local products is evident.

In view of the above, the first objective of this study was to evaluate B.C. white spruce [Picea glauca (Moench.) Voss.] foliage and western hemlock [Tsuga heterophylla (Raf.) Sarg.] bark powders as modifiers for plywood UF resins with purpose of improving glue bond durability (modifier action). A second objective was to examine the influence of these materials on UF glue properties with possibility of replacing wheat flour by foliage or bark (extender action).

The original intention of this work was to evaluate foliage and bark from Peruvian tree species. Efforts to obtain these materials failed and therefore Canadian products were used. However, it is hoped that results from this study will provide a basis for evaluation of Peruvian products in the near future.

2.0 REVIEW OF LITERATURE

2.1 Urea-formaldehyde Resin Characteristics

A UF resin is the condensation product of urea and formaldehyde. These can be polymerized to an effective resin under proper molar ratios, concentration, temperature, time and pH conditions (Rayner, 1965). By varying these factors a wide variety of UF resins can be made. Consequently, a UF resin is not a single compound of fixed chemical identity and its composition is not well defined. Steiner (1973), indicated that the formaldehyde-to-urea molar ratio governs to some extent the ultimate bond durability. For specific purposes, such as in plywood, veneering and assembly gluing, the molar ratio is usually 1U:1.75-1.9F and rarely above 1U:2F (Rayner, 1965). The UF mix also contains a substantial proportion of protein-starch extender, a minor proportion of lignocellulosic filler, water and an acid salt catalyst (Sellers, 1976).

UF resin reaction rate during the curing process is increased considerably by acids or substances capable of liberating acid when mixed with the resin. Setting consists of chemical curing and migration of the water which is partly contained in the liquid glue and partly chemically liberated from the resin during the condensation process (Kollmann et al., 1975).

Cured UF resins regardless of type or extension are weakened by continued exposure to temperatures from 49° to 70°C and the higher the temperature the greater the effect (Blomquist and Olson, 1957). Good quality UF glues produce good plywood grades and highly cold water resistant bonds.

The main advantages of UF resins are their low cost, compatibility with low cost extenders, nontoxicity and versatility. They can be formulated to cure at any temperature between 20 and 150°C and they can be readily modified or copolymerized with many materials to fit a variety of applications (Meyer, 1979). Other advantages of UF resins are their resistance to fungi, worms and termites, their lower sensitivity to wood moisture when compared to phenolics and the fact that they produce gluelines virtually invisible (Meyer, 1979).

Besides hydrolysis at high temperature, another disadvantage of UF is the pungent odor of formaldehyde released during manufacture and use of products.

2.2 Modifiers and Extenders for UF Resins

In this study the term modifier will be used to mean a material with inherent adhesiveness, that increases glue durability (resistance to moisture and heat). An extender is a material having some adhesive action added to an adhesive to reduce the amount of primary binder required per unit

area of adherend surface (CSA Standard 0112M-1977). On the other hand, a filler is defined as a non-adhesive substance added to an adhesive to improve its working properties, permanence, gap filling or other qualities (Shields, 1975).

Many studies concerned with UF have indicated that their resistance to high temperatures and humidity can be improved by modification with synthetic or natural materials. Modification of commercial UF by adding melamine and resorcinol showed that any fortification was better than the unmodified resin but no addition level was better than straight melamine (Blomquist and Olson, 1964). Polyvinyl acetate and blood used as modifiers also improved the durability of UF resin bonds under controlled conditions of temperature and humidity for five years (Gillepsie et al., 1964). The best performances were obtained by modifying UF with polyvinyl acetate at 46:54 ratio and with blood at 17:83 ratio. Use of modifiers at higher levels gave less satisfactory performance due to increased moisture sensitivity.

The addition of blood albumin also substantially improved the performance of UF bonds exposed to high temperatures and moisture (Thomas and Taylor, 1962). As the level of blood was increased shear strength values increased for both unextended and wheat flour extended resins. Organic modifiers, such as furfuryl, alcohol and

imidazolidinone have been evaluated at different levels of addition (Steiner and Chow, 1974). Relatively small amounts of modifiers added as monomers to UF resulted in increased wood-glue bond durability and in increased softening temperature of the cured resin.

The influence of other natural products as modifiers and extenders has been reported in numerous studies. Hirata and Mineura (1974) used various potato starches with UF. They indicated that apart from color and odor drawbacks these starches could satisfactorily substitute for wheat flour as extender. Rayner (1965) reported that large additions of starch make a UF glue sensitive to moisture and support mould. Wheat flour is the most accepted extender today but maize, potato and tapioca starches are still used in various parts of the world. Blomquist and Olson (1957) pointed out that wheat flour used as UF extender had no pronounced effects on heat resistance. It has been indicated, however, that addition of other materials, such as walnut-shell flour, improved the durability of Douglas-fir laminates (Steiner, 1973). Sawdust of various woods has been evaluated as plywood glue filler (Kubota and Saito, 1974). Results indicated the feasibility of using sawdust as filler for both UF and phenolic glues. Fine particleboard sander dust performed satisfactorily as phenolic extender (Knudson et al., 1978). Mineral fillers

are also used. Strickler and Sawyer (1974) developed four phenolic formulations using two types of attapulgite clays as the filler-extender system. Plant trials demonstrated the feasibility of using this material in commercial production.

Successful use of so many different materials as fillers, extenders and modifiers with UF proves the great versatility and compatibility of these resins.

Research on the use of bark or bark extracts as adhesive, extender or modifier has been carried out in several laboratories. McLean and Gardner (1952) indicated the possibility of using tannin extracts from western hemlock bark either with formaldehyde or PF as a plywood adhesive. Herrick and Bock (1958) developed thermosetting glues for exterior plywood by combining bark extracts with polymethylol-phenol. Formulations containing 49% bark extract, 34% polymethylol-phenol and 17% filler produced acceptable exterior grade Douglas-fir plywood. The bark of western hemlock has been recognized as a potential source of vegetable tannins for many years. Scott (1956) stated that the tannin content in western hemlock bark amounts 8 to 9%. Anderson et al. (1974) reported that when paraformaldehyde is added to white fir (Abies concolor Gord. & Glend.) bark particles and processed into a board, formaldehyde released during the hot-press cycle reacts in situ with

bark polyphenolic compounds forming a water resistant bonding agent.

The influence of untreated bark on both UF and PF formulations has been investigated. Hamada et al. (1969) indicated that addition of wattle (Acacia mollissima Willd.) bark powder to PF formed a mix with excellent flow properties and that setting time was shortened by bark addition. Imura et al. (1974) used the bark powder of Japanese larch [Larix leptolepis (Sieb. and Zucc.) Gord.] with UF for gluing birch (Betula spp.) boards. Bark powder proved effective in improving bond durability.

More recently, Steiner and Chow (1975) investigated factors influencing use of western hemlock bark extracts as adhesives. Bark age and method of extraction were found to influence adhesive quality. They pointed out that bark extracts offer potential for exterior grade particleboard and plywood, if extractive-instability problems are overcome.

The utilization of foliage as extender or modifier has not been investigated extensively. One of the few studies indicates that phenolic and carbohydrate substances in foliage have simpler, smaller molecular structures than wood and that these lower molecular weight components may provide greater chemical reactivity with synthetic resins (Chow, 1977). The same author points out that certain

foliage component blends may produce a high-performance polymer mixture with potential adhesive properties. Furthermore, the addition of foliage to an adhesive mix may have a humectant function influencing viscosity and preventing dry-out of the glue line during assembly. Chow (1977) also examined foliage as extender for both liquid and powdered PF resins. He concluded that foliage not only can be used as extender, but can also act as a partial replacement for the resin itself.

More recently, Chow, Steiner and Rozon (1979) reported on the efficiency of coniferous foliage as extender for powdered PF resin. They examined the adhesive potential of foliage without addition of PF; the influence of foliage content in a powdered resin system on the shear strength and internal bond in plywood-type laminations; and also fabricated experimental waferboard with foliage-phenolic resins. Results of these experiments reaffirm that foliage by itself has inherent adhesive properties. They also showed by scanning electron microscope (SEM) that pure foliage adhesive flows almost like a phenolic mix, and pointed out that this similar rheological property demonstrates compatibility of these materials as mixed bonding agents.

2.3 Factors Affecting Glue Extender Performance

The most widely used extender in interior UF formulations is wheat flour. Special wheat flours have been developed to optimize properties. In consequence, new materials that are to be used for this purpose should have, to a certain extent, similar characteristics.

The fundamental properties required of extenders is that they build and maintain a uniform viscosity and that they hold the glue on the wood surface. In addition, they should improve performance by increasing pot life and improving the bonding capacity of a specific quantity of mix solids (Robertson, 1966). Robertson (1974) indicated that when using wheat flour as extender it should meet specific requirements such as: Uniformity; Protein content maximum 10%; Ash content maximum 0.55%; pH about 6.0; Plain (no phosphates or bleaching); Low to medium water requirement; Fine particle size; Stable; Easy mixing; and Minimum lumping tendency.

Wheat is unique in that it is the only cereal containing significant quantities of the protein substance, gluten. Gluten has inherent adhesiveness and has an excellent capacity for building and holding viscosity in an extended mix (Robertson, 1979). Hill (1952) had previously indicated that the protein content of wheat is an indication of the amount of gluten present and that it is this gluten content

which determines its quality as an extender. Flour containing excessive gluten causes erratic viscosity behavior and forms sludge which obstructs glue flow. Furthermore, bleached and phosphated flours can also cause difficulty due to the treatment they have received. They may accelerate resin curing to a degree that impairs properties of that glue mix.

Extender particle-size has been indicated as influencing glue properties, especially viscosity and spreading. Coarse particle-size causes excessive adhesive thickening in the spreader and settles during storage (Knudson et al., 1978). Kubota and Saito (1974) reported that filler particle-size affects the temporary bonding strength of urea resin. Wood powder, with 90% of the particle size smaller than 400-mesh, mixed with UF gave plywood strength equivalent to that when wheat flour was used.

Stone and Robitscheck (1978) pointed out that such factors as particle-size, drying temperature, weight consistency and moisture content of extender materials have relative importance. The most critical factor is the inherent chemical nature of the material.

2.4 Factors Affecting Plywood Bond Quality

2.4.1 Veneer quality

Veneer moisture content, surface roughness, surface aging, density and lathe checks have been described as factors affecting plywood bond quality.

Veneer drying to a moisture content either too high or too low, seriously affects bond quality. Excessive moisture areas in the veneer cause steam pressure eruptions (blisters) of plywood laminates during or immediately after hot pressing. On the other hand, veneers subjected to excessive drying can develop "surface inactivation" which produces plywood of poor bond quality (Chow et al., 1973).

Veneer surface roughness is a significant factor in plywood gluing. Varying roughness causes differences in optimum glue spread and also requires higher pressure to obtain equal surface contact area. Surface roughness due to mechanical preparation can in certain situations increase bond strength by interlocking when tested in shear. Increasing roughness, however, produces inevitably thicker bonds with more defects and localized stresses which in the end reduce strength. Marian et al. (1958) found that strength of edge glued bonds increased with surface roughness until a point at which the simultaneously decreasing strength of the wood and increasing porosity

caused the wood to break. Beyond this point, further increase in roughness reduced the shear strength. Lately, Hancock (1980) found that wood failure percentage is affected also by the degree of veneer roughness. Smooth veneer had approximately 17% higher wood failure than the average of the medium and rough surface veneers. The same relative effect upon wood failure with respect to roughness was seen regardless of the type of test.

Lathe checks are known to reduce veneer quality and influence plywood quality. Palka (1964) found that plywoods made with sawn-veneers (no lathe checks) had an average shear strength 1.5 times higher than plywoods made with rotary cut veneers. Chow (1974) gave photographic evidence that the behavior of plywoods made with rotary cut veneers under load is completely different from that of sawn-veneer plywoods. He also indicated that shear strength was greatly influenced by the depth of glue penetration into lathe checks.

Aging of the wood surface is another factor affecting bond quality. Stumbo (1964) suggested four possible mechanisms that influence surface gluing properties due to aging: (1) Migration to the surface of extraneous material that is detrimental to wood gluability; (2) Chemical changes of the wood substance or of the extraneous material at the surface, producing a less glueable surface;

(3) Decreases in the surface free energy due to adsorption of airborne contaminants and chemical changes or molecular rearrangements; and (4) Decrease in strength of the wood fibers due to oxidation. The same author in a study of Douglas-fir and redwood [Sequoia sempervirens (D. Don) Endl.] surfaces protected against contamination found bond strength reduced by as much as 12 to 50% over exposure periods ranging from 3 to 5 months. Northcott et al. (1959) reported little difference when gluing Engelmann spruce (Picea engelmannii Parry) veneer stored 30 days and that stored only three days. The above indicates that bond quality decreases as the veneer age increases and, therefore, the time elapsed between peeling and gluing should be as short as possible.

2.4.2 Glue viscosity

Glue viscosity is a rough index of resin molecular size or degree of polymerization which affects flow, transfer, penetration and wetting (Rice, 1965). After glue has been spread on wood, it must pass through several flow stages before a strong bond can be formed. It must: (1) Flow laterally to form a continuous film; (2) Transfer from the wood surface on which it was spread to the opposite, unspread surface; (3) Penetrate into both surfaces of the joint; (4) Wet the wood surface; and (5) Solidify

into a strong substance (Brown et al., 1952). These stages, except the fifth, involve flow and, therefore, are greatly influenced by adhesive fluidity.

High viscosity offers resistance to spreading and reduces glue flow. On the other hand, if a condition of too low viscosity exists, then excessive glue migration away from the surface occurs and this may affect bond quality. Viscosity influences eventual bond quality. Rice (1965) has indicated the dependence of bond quality on viscosity. High viscosity extended UF resins produced thicker gluelines, which were significantly more durable than those made with low unextended resins. Ramos Garcia (1965), however, obtained higher shear strength values with lower viscosity PF resins than with higher viscosity ones.

The effect of viscosity on bond quality appears controversial. This effect should not be viewed independently but along with other factors, such as a resin type, wood moisture content and assembly and pressing times.

2.4.3 Glue application, assembly time and pressing

Spread levels and mix formulations vary according to glue type and wood. There are useful maximum and minimum limits to spread level. Hill (1952) indicates that when hot pressing these limits are 11 to 16 kg/100 m² (24 to

35 lb/1000 ft²) for unextended resins and 16 to 20 kg/100 m² (35 to 44 lb/1000 ft²) of single glueline for extended ones. High spread levels are prone to excessive squeeze-out and blister formation due to high glueline moisture. In addition, higher amounts of water must be absorbed by the wood or it must be evaporated for complete curing, thus longer pressing time is necessary. On the other hand, if the spread level is too low the water diffuses rapidly into the wood and adhesion is reduced (Kollmann et al., 1975).

Assembly time is the length of time elapsed between glue spreading and pressure application. This is divided as open assembly time, where the spread glue is exposed on open veneer, and closed assembly time, the period between the making up of an assembly and the application of pressure. Assembly time allows for some moisture absorption by the veneer and some reduction in viscosity due to moisture loss. The particular characteristics of a glue system have considerable effect on assembly time. Veneer density, moisture content and spread level also play important roles. Dense veneers retain more water in the glueline than do less dense veneers and high spread levels are conducive to longer assembly times, whereas low spread levels are associated with shorter assembly times (Hill, 1952).

The effects of resin age and veneer moisture content

on assembly time have been reported (Marra, 1964). A fresh mix with a short assembly time tended to produce a starved state on high moisture veneer, but was optimum for drier veneer. As assembly time increased, however, the optimum passed from dry veneer to higher moisture veneer. Furthermore, as the age of the mix increased, higher moisture veneers and shorter assembly times were required.

Driehuyzen and Wellwood (1960) investigated the effects of glue room temperature and humidity on open assembly time. They indicated that at the same temperature, high relative humidities permitted longer assembly times than low relative humidities. Lowering the temperature and increasing the relative humidity simultaneously resulted in a substantial increase in maximum allowable open assembly time.

Adequate pressure is required in gluing for various reasons, such as to: (1) Bring surfaces into as close contact as possible, thereby producing a thin glueline, squeezing out excess glue and increasing penetration to undamaged portions of the adherend; (2) Ensure good transfer to the unspread veneer face; and (3) Maintain good contact between veneers of normal roughness during final glue cure. Pressure is applied according to wood compressive strength. Pressures usually applied are 200 psi

for Douglas-fir. Excessive pressure leads to compression losses in plywood thickness (Kennedy, 1965).

During pressing, heat is applied for various reasons, such as to (1) Increase rate of chemical reaction in the curing of thermosetting glues; (2) Decrease viscosity and increase penetration; (3) Increase wood plasticity; and (4) Remove solvent from the glueline by evaporation, diffusion or capillary movement (Kollmann et al., 1975). Heating of the wood involves simultaneous heat and mass transfer peculiar to wood. Changes in temperature induce moisture movements in wood. For optimum bonding, veneer should contain a definite amount of moisture.

Fisher and Benseid (1969) have indicated that with short hot press times the glue does not receive a sufficient quantity of thermal energy to attain a complete cure; but at long hot press times several factors can lower panel quality. The veneer can be over-dried causing not only severe interfacial stresses while in the press, but severe stresses during reconditioning of the panel to the desired moisture content. Also by producing a complete cure in the hot press instead of allowing the cure to continue in a hot stacking period, stresses may be introduced in the glueline itself.

Chow et al. (1973) indicated that the curing temperature for a glueline depends on the adhesive used among other factors. Inadequate curing temperature and insuffi-

cient pressing time are causes for undercured bonds. They also reported that with phenolic resins a minimum inner glue-line temperature of about 120°C is necessary to pass the CSA wood failure standard when the vacuum pressure-soak method of testing is used.

2.5 Glue Cure Indicators

Analytical methods, such as ultraviolet spectroscopy (UV), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and other techniques are useful for determining degree of cure, curing properties and thermal stability of thermosetting resins.

Chow and Hancock (1969) developed a simple spectrophotometric method for measuring the degree of cure of phenolic resins. They indicated that this method is good for predicting bond undercure and durability. In addition, the influence of pressing time and temperature on glue bond formation can be determined.

Differential thermal analysis (DTA) has been found useful for tracing directly the chemical reactivity of a glue. Chow and Steiner (1975) also examined the thermal reactions of UF by DTA during various stages of resin synthesis. The effects of ammonium chloride concentration, storage time and addition of extra urea also were examined. They concluded that the exothermic peak temperature of UF

in the presence of ammonium chloride catalysts is important to the pot life, assembly time tolerance and curing of the resin.

Chow and Steiner (1979) compared differential scanning calorimetry (DSC) thermograms of both liquid and powdered commercial PF resins. They found that the mechanism of cure for these resins is different.

2.6 Some Aspects of Wood Adhesion

Adhesion is a complex science involving chemical, physical and mechanical principles. The wood bonding process is especially complex, because the adherend is a heterogeneous system. The surface of wood is usually weakened by tools or exposure and the glue has to penetrate beyond the surface to form a bond. In hot-setting operations the situation becomes even more complex because the glue viscosity changes, wood extractives may migrate to the surface and intrinsic moisture steams the surface (Meyer, 1979).

Brown et al. (1952) indicated that in wood bonding two types of adhesion operate as: (1) Mechanical adhesion caused by anchorage resulting from hardened tentacles of glue extending into the wood; and (2) Specific adhesion caused by anchorage resulting from forces of adhesion acting between molecules and atoms of the wood and glue.

The mechanism of mechanical adhesion is explained by assuming that the glue, while still in liquid form penetrates into the wood cell cavities. Thereupon, it solidifies and the bond strength is due, at least in part, to interlocking of the two solids, the wood and the glue embedded in the wood (Brown et al., 1952). When referring to mechanical adhesion, Truax (1929) and other researchers have pointed out that mechanical adhesion alone would be quite inadequate to account for the strength of wood joints. Marian and Stumbo (1962) indicated that mechanical adhesion only contributes about 10 to 20% of the total adhesive strength. Mechanical adhesion can operate with wood, depending on joint type and surface condition of the adherend member. Rough or damaged surfaces will influence mechanical adhesion, but for smooth and undamaged surfaces this influence is minimal.

Specific or chemical adhesion is explained on the basis of molecular or atomic attraction between the adhesive and the wood surface. Specific adhesion is caused by primary valence forces or secondary valence (van der Waal's) forces (Marian and Stumbo, 1962). Kollmann et al. (1975) stated that primary valences, ranging from 10 to 100 or more k cal/mole, are strong forces of attraction between atoms. They determine the structure of molecules and appear in some chemical processes. They are not important

for the phenomenon of adhesion. The weaker secondary valences (2 to 4 k cal/mole) decide the amount of adhesion. Another author (Zisman, 1963) remarked that adhesion is caused by forces between molecules in or near the surface of the two contacting materials and that these are primarily of van der Waal's and hydrogen bonding types.

Hydrogen bonding is one type of secondary chemical bonding in which hydrogen ions are mutually shared by reactive polar groups, usually carboxyl or hydroxyl. Klein (1975) has indicated that the potential for hydrogen bonding depends upon the number of reactive groups in resin and wood molecules, wettability of the adhesive and its ability to cure in place with a minimum of shrinkage and internal stresses, while reactive sites on the resin and wood molecules are sharing hydrogen ions.

In analyzing the factors that influence the bonding process in wood, Marra (cited in Meyer, 1979) has indicated that the true bond forming potential of a glue must involve both bond formation and bond performance. Bond formation includes establishing adhesion and achieving strength. Bond performance is reflected in bond strength and permanence. He explained that the conditions under which these factors combine involve four systems: (1) The basic chemical, physical and mechanical natures of the liquid and solid glue; (2) The corresponding properties of the adherend;

(3) The consolidation conditions, including pressure, temperature, humidity and time; and (4) The exposure or service conditions of the final product.

2.7 Assessing Plywood Bond Quality

The Canadian Standards Association (CSA) uses percentage wood failure as the basis for assessing plywood bond quality. CSA defines wood failure as "the area of wood fibre remaining at the glue line following completion of the specified shear test. Wood failure is determined by means of visual examination and expressed as a percentage of the unit test area." The reasoning behind the concept of wood failure is that the test specimen must have a glue bond strength at least equal to that of the wood in the specimen (Yavorski et al., 1955).

The validity of using percentage wood failure has been questioned in several cases. Marian and Stumbo (1962) pointed out that shear tests for wood are unsuitable because of the variation in density from log to log which makes wood failure an arbitrary figure. Wood failure as such is a function of springwood-summerwood ratio and distribution. Plywood made of veneers from a fast-grown log will show definitely higher wood failure percentages than that from a slow-grown log. Shen (1958) indicated that certain variations in the wood, glue, gluing procedure or in testing

and measurement methods may cause wood failure to vary considerably. In practice, the reading of percentage wood failure is a highly developed skill subject to operator variability.

Some countries (Japan, Germany) use shear strength as the sole criterion for assessing plywood bond quality. Shear strength is defined in terms of the ultimate shear strength (N/mm^2 , lb/sq in) required to break a test plywood specimen in tension shear.

The relationship between wood failure and shear strength is not well defined. Northcott (1952, 1955) postulated that there was poorer correlation between breaking load and service life than between wood failure and service life. Shen (1958) indicated that breaking load in Engelmann spruce (Picea engelmannii Parry) plywood was a better indicator of bond quality than wood failure. Palka (1964) found that an increase of shear strength was associated with higher wood failure. Chow and Warren (1972) found that wood failure is a more sensitive measure of glue bond undercure than was shear strength. Chow (1974) explained that in properly assembled plywood with bonds having an optimum degree of cure, final shear strength has no direct relationship with percentage wood failure, but is intimately influenced by the depth of lathe checks or veneer quality. Chow and Chunsi (1979) derived an intrinsic relationship

between shear strength and wood failure which was applicable to 50 South Asian hardwoods (SG 0.33 to 1.01). They indicated that if a sound wood substrate is used, the wood failure percentage is a good representation of bond strength, regardless of its direct or indirect correlation with absolute strength.

From the literature above, it appears that a relationship between shear strength and wood failure may exist. This subject is still controversial. It has been suggested (Chow, 1974; Chow and Chunsi, 1979) that adoption of both shear strength and wood failure as criteria in plywood-bond quality control could be the best safeguard for ensuring a satisfactory bond.

3.0 MATERIALS AND METHODS

3.1 Experimental Plan

The experimental plan included four variables: Two wheat flour extended UF resins; Two modifiers; Two pressing times; and Three modifier addition levels. The plan was as follows.

Two UF resins: 1) Commercial plywood UF resin (UF);
and a

2) Laboratory synthesized, low molecular weight UF resin (Ufi).

Two modifiers: 1) Ground white spruce foliage; and

2) Ground western hemlock bark.

Two pressing times: Six; and Ten min.

Three modifier addition levels: 15; 30; and 45%.

The experiment was divided into two stages.

The first stage comprised evaluation of foliage and bark as modifiers for the commercial UF resin. The above variable combinations gave 12 treatments, two controls of wheat flour extended commercial UF resin were used giving a total of 14 treatments. Two panels were made for each treatment.

The second stage evaluated foliage and bark as modifiers for a laboratory synthesized low molecular weight UF resin (Ufi). The variable combinations used gave four treatments,

two controls of wheat flour extended low molecular weight UF resin were used giving a total of six treatments. Only 30% modifier addition was evaluated in this case.

From both stages a total of 20 treatments and 40 plywood panels were included in the study.

Plywood panels were prepared under the following conditions:

- 1) Douglas-fir [Pseudotsuga menziesii (Mirb.) Franco] veneer, 3.17 mm thickness;
- 2) Five-ply, 38 x 38 cm test panels;
- 3) Glue spread 32 kg/100 m² (70 lb/1000 ft²) of double glueline;
- 4) Closed assembly time 20-min;
- 5) Pressure 1.38 MPa;
- 6) Pressing times 6 or 10-min;
- 7) Platen temperature 149°C; and
- 8) One panel per opening.

Bond quality was evaluated by:

- 1) Dry test, following conditioning to atmospheric EMC;
- 2) Vacuum pressure-one cycle;
- 3) Vacuum pressure-five cycles; and
- 4) Boil-dry-boil test.

Wood failure percentage (CSA 0121-M1978) and shear strength data were used to assess bond quality. Wood failure was read by the author of the study.

3.2 Veneer

Dry, rotary-cut, 3.17 mm thickness, grade 'A' Douglas-fir veneers obtained from MacMillan Bloedel Ltd. were supplied by Forintek Canada Corp. (Western Forest Products Laboratory, Vancouver). These were cut into 38 x 38 cm squares and stored in a controlled temperature-humidity room which approximated 50% relative humidity (dry bulb 26.7°C and EMC of about 6%). Prior to gluing, moisture content of individual veneers was checked by using an electronic moisture meter (Moisture Reg. 'L' Co.). A randomly selected sample of 50 veneer pieces was used for these measurements (Table 1).

Veneer thickness variation was estimated prior to gluing by using an apparatus activated by air pressure and equipped with a micrometer (0.001-in accuracy). At random, fifty 38 by 38-cm veneer pieces were selected for these measurements. Veneer thickness was obtained by averaging five readings on each piece (Table 1).

Veneer roughness was estimated prior to gluing by means of a visual veneer roughness scale developed by Northcott and Walser (1965). Randomly, fifty 38 by 38-cm veneer pieces were used for this test (Tables 1 and 2).

The depth of lathe checks was measured on a 2.54-cm cross section from the deepest point of lathe check. Depth of the three longest lathe checks was averaged and divided

by veneer thickness to give a percentage depth of lathe check. Fifty randomly selected pieces (38 by 10-cm) were used for this test. Each piece and section was submerged in a dye solution (gential violet) and then lightly sanded. This permitted the stained part to be more easily observed and provided accurate measurements (Table 1).

Lathe-check angles were measured on a 2.54-cm cross section with a transparent protractor. Angle of the three longest lathe checks was averaged to represent the piece. The same veneer pieces used for lathe-check depth were used for these measurements (Table 1).

3.3 UF Resins

The commercial standard UF resin (Casco UF 109) is a high solids ($63 \pm 2.0\%$), aqueous resin solution. It is a clear to slightly cloudy viscous liquid when fresh, becoming increasingly cloudy on storage. Casco UF 109 resin, as indicated by the manufacturer meets industrial need for a durable glue that is water resistant, fungus proof and can be used in gluing both hardwoods and softwoods.

The laboratory synthesized low molecular UF resin (UFi) was used in this study on the assumption that it could provide a system with potential for chemical reaction with foliage and bark low molecular weight phenolic compounds. It is generally agreed that the size of polymer molecules increase

at different stages of condensation-polymerization. Also, molecular growth occurs at the expense of reactive (methylol) groups, as the degree of polymerization increases the number of free reactive groups decreases (Parkes and Taylor, 1966). Thus, a low molecular weight resin, product of low degree of condensation should have more available reactive groups to undergo reaction with eventual modifiers.

The low molecular weight UF resin (UF1) of molar ratio F/U=2 was prepared by placing 1500 g of 46.3% formaldehyde solution and 695 g of urea in a reaction vessel, and pH was adjusted to about 8 with 50% sodium hydroxide (NaOH) solution. The solution was heated to 70°C and the temperature was maintained 45-min. The solution was made slightly acidic (pH about 6) with 10% HCl and then refluxed for 30-min. Finally, the mixture was cooled and neutralized with NaOH solution. Total solids content was about 63%.

3.4 Foliage and Bark

White spruce foliage (95% needles) and western hemlock bark dried and pulverized were provided by Forintek Canada Corp. These materials were collected approximately one year before used in this experiment. Foliage was collected from a commercial logging site (Princeton area) in the interior of British Columbia while bark was collected from Eburne Sawmills Division, Vancouver, B.C. Prior to use as

modifiers, foliage and bark were air-dried and put through a hammer mill, they were then oven-dried at $103 \pm 2^{\circ}\text{C}$ until moisture content was about 8%. Finally, both materials were ground using a Pallman grinder 'L' 18. Moisture content of foliage and bark was checked prior to use in the glue mixes by oven-drying two five g samples of powders (Table 3).

Particle-size distributions of foliage and bark powders were determined by screen analyses using a shaker (100, 200 and 325-mesh screens) with 100 g samples. The screens were first shaken for 15-min and the weight of sample retained on each screen was recorded. The screens were then re-stacked, shaken for another 15-min and weighed again. The average value of two analyses was recorded.

Foliage and bark pH was determined by using a standard Corning pH meter 125. The tests were conducted by mixing five g sample of dry, powdered material and 200 ml of freshly distilled water. The average pH value of two measurements was recorded (Table 3).

Ash content data on foliage and bark was obtained from previous research at Forintek Corporation (Table 3). The tests were performed in accordance with ASTM D 1102-56 (1977).

3.5 Glue Mix Properties

The commercial plywood UF glue mix was prepared following the manufacturer's instructions and this was used within the recommended working pot life. The same instructions were followed to prepare all other mixes including the laboratory synthesized resin. Foliage and bark were added to the mix at 15, 30 and 45% levels based on resin solids content (or 20, 40 and 60% based on extender content). The standard mix formulation is given in Appendix I.

Glue mixing was performed with a mechanical-electrical mixer equipped with a steel stirrer. Stirrer rotation speed was 700 r.p.m. A five gallon plastic container was used for mixing glue components.

Viscosity measurements were performed in accordance with ASTM D2556-69 (1977) one-hr after mixing at $22 \pm 1^{\circ}\text{C}$. A Brookfield synchroelectric LVF viscometer with spindle No. 4 at 30 r.p.m. was used. A 600 ml beaker and 400 ml glue mix were used for this test.

PH was determined using a standard Corning pH meter 125 four-hr after mixing. Prior to pH determination, the mix (300 ml) was stirred manually to reachieve homogeneity

Density was determined four-hr after mixing at $22 \pm 1^{\circ}\text{C}$, using a 1000 ml graduated cylinder tared and 1000 ml mix. Density was calculated from the weight/volume ratio.

Gelation time was measured four hours after mixing.

Fifteen grams of mix were placed in a 25 ml test tube and stirred regularly while suspended in a hot water bath at 60°C. The gelation time as average value for two samples was recorded for each mix. Mix stability was determined by viscosity measurements at one, 24- and 48-hr. A Brookfield synchroelectric LVF viscometer with spindle N° 4 rotated at 30 r.p.m. was used.

3.6 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to examine curing properties of glue mixes prepared for the study. The method depends on measuring differential power or heat input necessary to keep a sample and a reference substance isothermal as temperature is changed linearly (Bauer et al., 1978).

All differential scanning calorimetry analyses were performed on a Perkin-Elmer DSC-2 instrument. A sample of about 2 mg was placed in an aluminum sample pan and sealed with a cover lid. The sample was then heated in a DSC sample cell to 250°C at a constant rate of 10°C/min (Figure 1). Time required for each analysis was approximately 30-min.

3.7 Plywood Manufacture

The glue mixes were spread at about $32 \text{ kg}/100 \text{ m}^2$ ($70 \text{ lb}/1000 \text{ ft}^2$) of double glueline. This is within the limits ($30 - 40 \text{ kg}/100 \text{ m}^2$) used in industrial practice and recommended by Hill (1952). A mechanical spreader was used for glue application. Five-ply, 38 by 38 cm panels, were prepared. Each panel was comprised of five randomly selected veneers. Standard plywood shear specimens were cut from each panel to have lathe checks pulled closed. Chow (1974) found when testing white spruce plywood that shear strength was lower for specimens in which lathe checks were pulled open rather than closed. For each treatment, two plywood panels were assembled. Each panel was coded with respect to glue type and pressing time, modifier and addition level.

Twenty min closed assembly time (CAT) was used. This is within the limits (10 to 30-min) used in hot pressing operations. Rose (1957) reported that when veneers of moderate moisture content (5 to 8%) are used, UF glue develops maximum bond strength at CAT of 20 to 30 min.

Two pressing times, 6 and 10-min, were used. In industrial operations pressing time ranges from 6 to 10-min. In this case both times were used to insure proper glue cure. Following industrial practice a press pressure of $14 \text{ kg}/\text{cm}^2$ (200 psi) and 149°C platen temperature were used. Chow et al.

(1973) reported that at about 150°C platen temperature the inner center glueline reaches 120°C. They also indicated that with phenolic glues a minimum inner glueline temperature of 120°C is needed to pass the CSA 80% wood failure standard, when the vacuum pressure method is used.

3.8 Bond-Quality Testing

Shear test specimens were prepared from each test panel in accordance with CSA Standard 0121-M1978 for Douglas-fir plywood. An average of 40 shear specimens were obtained from each panel, from which ten specimen were randomly assigned for each of the three conditioning cycles. Shear specimens were coded by panel and experimental variables.

One set of specimens was tested following conditioning to ambient temperature and relative humidity (dry test). A second set was placed in a pressure vessel and immersed in cold tap water. A vacuum of 85 KPa (635 mm mercury) was drawn by water vacuum and maintained for 30-min, followed immediately by application of 450 to 480 KPa (65-70 psi) pressure. Specimens were then removed from the vessel and tested while still wet.

The vacuum pressure-five cycle conditioning is not included in the CSA 0121-M1978. It was carried out here as a treatment intermediate between vacuum pressure and boil-dry-boil tests. It was assumed that this would better

indicate plywood bond durability, especially with UF glue mixes which are known to have good water resistance. The method follows the same procedures as the vacuum pressure test, except that it involves five vacuum pressure-drying (at 50°C) cycles. Samples were tested wet. The fourth set of specimens was boiled for four-hr and then dried for 20-hr at $63 \pm 3^\circ\text{C}$. Specimens were boiled again for four hours, cooled in room temperature water and tested while wet.

Shear test specimens representing 40 panels were tested by tension loading to failure in a standard Globe shear testing machine. This was operated at a loading rate of 272 to 454 kg/min. Following shear test, wood failure was read after the wet specimens were oven-dried to prevent reading errors since water makes wood fibers transparent.

3.9 Statistical Analyses

Analysis of variance (ANOVA) were performed on both shear strengths and wood failure percentages. This allowed for comparison among treatments. The Duncan's Multiple Test was used to test for significant differences between treatments.

To facilitate interpretation of results, the same number of shear test specimens (20) was tested for all treatments. Each treatment was coded for identification as shown in Appendix II.

4.0 RESULTS

Thermograms of the commercial UF resin with wheat flour, 30% foliage and 30% bark, are illustrated in Figure 1.

Foliage and bark powder properties such as moisture content, ash content, pH and particle size distribution are presented in Table 3.

Glue mix physical properties such as viscosity, pH, density and gelation time are presented in Table 4.

4.1 Modified Commercial UF Glue

Table 5 summarizes average shear strengths and wood failure percentages for the 14 glue mix (M) and pressing time (PT) treatment combinations following three conditioning treatments. Figures 2, 3 and 4 illustrate results of dry, vacuum pressure-one cycle and vacuum pressure-five cycles as shear strengths and wood failure percentages. The boil-dry-boil test resulted in complete delamination of shear test specimens. No values were recorded.

4.2 Modified Laboratory UF Glue (UFi)

Table 6 summarizes average shear strengths and wood failure percentages for the six treatment combinations of M and PT following three conditioning treatments. Figures 5, 6 and 7 illustrate results of dry, vacuum pressure-one cycle and vacuum pressure-five cycles as shear strengths

and wood failure percentages. As in the case of the commercial UF glue, the boil-dry-boil test resulted in complete delamination of shear test specimens.

4.3 Statistical Analyses

Results of dry-shear strength and wood failure percentage analysis of variance (ANOVA) for treatments bonded with the commercial UF glue are summarized in Table 7. The table shows the significant main and interacting effects at 0.01 and 0.05 probability levels. The interactions M x PT are depicted in Figure 8.

Table 8 summarizes ANOVA results of vacuum pressure-shear strengths and wood failure percentages for treatments bonded with the commercial UF glue. The interactions M x PT are depicted in Figure 9.

Table 9 summarizes ANOVA results of vacuum pressure-five cycles shear strengths and wood failure percentages for treatments bonded with the commercial UF glue. The interactions are depicted in Figure 10.

Similarly, Table 10 summarizes ANOVA results of dry shear strengths and wood failure percentages for treatments bonded with the laboratory UFi glue. Table 11 summarizes ANOVA results of vacuum pressure-one cycle shear strengths and wood failure percentages for treatments with the UFi glue. Finally, Table 12 summarizes ANOVA results of vacuum

pressure-five cycles shear strengths and wood failure percentages for treatments with the UFi glue. The interactions $M \times PT$ are depicted in Figures 11, 12 and 13.

Tables 13 and 14 present results of Duncan's multiple range test for treatments bonded with the commercial UF glue. Tables 15 and 16 present results for treatments bonded with the UFi glue.

5.0 DISCUSSION

5.1 Foliage and Bark Properties

As shown in Table 3 white spruce foliage had a slightly lower particle-size distribution than western hemlock bark. Foliage had 81.8% passing through the 200-mesh screen while bark had 78.3%. When dried to a moisture content below 10%, both materials were easily pulverized to the fine particle-size. The type of grinder could affect foliage and bark results. Chow (1977) compared Pallman ring grinder efficiency with that of a Sprout-Waldron grinder and found that the former was much more effective in grinding foliage to particle-size below 200-mesh. The Pallman grinder was used in this study.

As indicated earlier the particle-size of materials used as glue extenders or fillers influences glue physical properties (Knudson et al., 1978; Kubota and Saito, 1972; Stone and Robitscheck, 1974). Fine particle-size is reported to be a requirement for high quality extenders. Coarse particle-size affects glue viscosity, spreadability, pot life and ultimately bond quality. The screen analyses tests carried out in this study indicated that both foliage and bark can be ground to a fine particle-size suitable for use as extenders or fillers.

The moisture contents of white spruce foliage and

western hemlock bark were 6.2 and 8.0%, respectively (Table 3). Higher moisture contents may affect glue properties especially viscosity.

As shown in Table 3 the pH of white spruce foliage and western hemlock bark were 4.3 and 4.7 respectively. Chow (1977) reported a similar pH for white spruce foliage. The pH of foliage and bark are acidic and compatible with UF resins which are typically acid curing resins.

The ash contents of white spruce foliage and western hemlock bark were 3.7 and 2.3% respectively (Table 3). Low ash content in an extender is a quality criteria and a selection factor. Robertson (1974) pointed out that for wheat flour extenders an optimum ash content should be about 0.55%. Other materials used as glue extenders such as ground oat, rice and corncob hull residues have ash contents in the range of 8 to 20% (Stone and Robitscheck, 1974). The ash contents of foliage and bark are relatively low and adequate for use with glue systems.

5.2 Modified Commercial UF Glue Properties

As shown in Table 4, mixes UF-F15 and UF-F30 gave lower viscosities than the control mix. The viscosity of UF-F30 was similar to that of the control. Higher foliage addition (UF-F45) produced higher viscosity than the control and exhibited unsuitable flow properties. This mix was

still spreadable after two-hours but showed a tendency to lump during spreading.

The mixes with bark additions UF-B15 and UF-B30 exhibited higher viscosities than the control mix but were suitable for spreading. Mix UF-B45, as in the case of foliage additions, had too high a viscosity and was unsuitable for spreading. It has been reported that bark addition to UF resins increases glue viscosity and that this is more pronounced when highly condensed UF resin is used (Hamada et al., 1969).

It was observed during viscosity measurements that all mixes exhibited a drop in viscosity when subjected to constant shearing but reached their final value within one-min. This phenomenon is known as thixotropy and can be attributed to the presence of wheat flour and foliage or bark in the mix.

The importance of glue viscosity was reviewed earlier. Optimum viscosity ensures proper glue flow and helps glue transfer from the spread veneer surface to the unspread surface. It also affects glueline thickness and glue penetration into the veneer surfaces.

Results from this study indicate that large additions of untreated foliage and bark powder produce high and unsuitable viscosities. This occurs because large additions absorb considerable amounts of water from the mix, thus

increasing viscosity. It has been found (Steiner, 1980) that white spruce foliage and Douglas-fir bark water absorbency rate is about 180%, while wheat flour rate is 80%. The higher viscosity produced by bark additions compared with lower viscosity by foliage additions indicates that bark has a greater chemical interaction with the UF resin. Evidence of considerable reactivity between western hemlock bark tannin constituents and formaldehyde has been reported (Hamada et al., 1969; Steiner and Chow, 1975). In the case of foliage additions, Chow (1977) reported that foliage might have a humectant function that influences glue viscosity. Also, Chow et al. (1979) found that a mix of pure foliage exhibits similar flow properties to phenolic resin. This foliage humectant property may explain the lower viscosity produced by foliage additions up to the 30% level.

As shown in Table 4 the mixes with foliage and bark additions had lower densities than the control mix. In both cases the glue density was found to decrease with increased addition. The results suggest that, since the mixes with foliage and bark additions have lower density than the control, these mixes will give more glue volume per unit area than the control when spread at equivalent levels. Also, these mixes may have an improved gap filling property because of their greater volume.

Table 4 shows that mixes with foliage and bark additions had lower pH values than the control mix. This was expected since foliage and bark have 4.3 and 4.7 pH values, respectively. Mix pH decreased with an increase of addition level. It has been indicated that glue viscosity and pot life are dependant on rate of pH fall with time (Rose, 1967).

Gelation time provides a means for evaluating setting rate and potential speed of reaction of crosslinked polymer systems during their transformation from liquid to solid phase (Steiner and Chow, 1975).

It is shown (Table 4) that mixes with foliage exhibited slightly longer gelation times than the control mix. Conversely, mixes with bark gave shorter gelation times than the control. From these results it appears that higher bark additions increased glue reactivity, thus shortening gelation time.

In a similar study with phenolic resins Hamada et al. (1969) reported that glue setting time was shortened by bark addition.

Glue mix stability as indicated by viscosity measurements at one-hour, 24 and 48-hr after mixing is shown in Table 4. Mixes UF-F15 and UF-F30 had a significant viscosity increment after 24-hr but were lower than the control. Mix UF-F45 had too high a viscosity which indicated low mix stability. Mixes with bark additions UF-B15 and UF-B30

also showed substantial increase in viscosity but remained workable under agitation. Mix UF-B45, as with foliage, developed excessively high viscosity which made the glue unworkable after 24-hr.

Over a period of 48-hr mixes UF-F15 and UF-F30 viscosities increased further but were still workable. Mix UF-F45 was so thick that viscosity measurements were not possible. Mixes UF-B15 and UF-B30 had higher viscosities than those of UF-foliage mixes and were similar to the control. The results indicate that 48-hr after mixing, foliage additions UF-F15 and UF-F30 exhibited better stability than the control mix. Mixes UF-B15 and UF-B30 exhibited similar stability to the control. Large additions of foliage and bark produced mixes with low stability, unworkable after 24-hours.

From the results it appears that glue pot life is dependent to a certain extent on the initial viscosity, mix formulation and rate of pH fall.

5.3 Differential Scanning Calorimetry

Chow and Steiner (1975) investigated the exothermic reaction of UF resin. Supported by results from differential thermoanalysis, thermogravimetric analysis, infrared spectra and softening temperature measurements they indicated that the exothermic peak is associated with resin cure. The endothermic peak is related to the heat of water evaporation.

As shown in Figure 1 the thermogram for the UF resin shows an exothermic peak at 64°C and an endothermic peak at about 100°C . The UF-wheat flour thermogram shows the peaks shifted to a higher temperature, exothermic at 82°C and endothermic at 116°C . Foliage addition slightly shifted the exothermic peak (96°) and the endothermic peak (120°C). UF-bark exhibited a similar thermogram to UF-foliage.

The slight temperature shift to the exothermic peak with foliage and bark additions may be important to glue pot life. Increased exothermic peak temperature may retard glue pre-cure, since higher energy is needed to initiate curing. Figure 1 also shows the influence of the glue extender. The exothermic peaks of UF-wheat flour, UF-foliage and UF-bark mixes occur at higher temperatures than that of the UF resin alone. This suggests that extenders improve glue assembly time tolerance and pot life.

5.4 Bond Quality of Modified Commercial UF glue

5.4.1 Dry test

Figure 2 and Table 5 shows that treatments with foliage additions (UF-F15-10, UF-F45 at 6 and 10-min PT) gave higher shear strengths than the control while treatments with 30% foliage at 6 and 10-min pressing time (PT) gave similar strengths to the control. Bark additions, with exception of treatment UF-B15-10, produced higher shear strengths

than the control.

The analysis of variance (ANOVA) for the shear strength data (Table 7) shows the interaction between glue mix (M) and pressing time (PT) as highly significant. This interaction (Figure 8), indicates that there was a different response among glue mixes to PT levels. Except for treatment with 15% foliage, PT did not appear to influence shear strength of treatments bonded with UF-foliage glue. In the case of bark, higher shear strengths were produced at 6 than at 10-min PT.

In general, treatments with foliage (UF-F15-10) and bark (UF-B45-6) gave the highest shear strengths at 2.08 MPa (302 psi) and 2.02 MPa (293 psi). Duncan's multiple range test for multiple comparisons (Table 13) indicates that these results were not significantly different at the 0.05 probability level. Treatments UF-C-6 (Control), UF-F15-6 and UF-B15-10 gave the lowest values at 1.48 MPa (214 psi), 1.55 MPa (225 psi) and 1.50 MPa (217 psi), respectively.

Figure 2 and Table 5 also show that one treatment with foliage (UF-F30-6) gave higher wood failure percentage than the control. Treatments with bark additions (UF-B15-10, UF-B30 at 6 and 10-min PT) gave higher wood failure percentages than the control.

The ANOVA for the dry-wood failure data (Table 7) shows, as in the case of the shear strength test, that the

interaction M x PT was highly significant. Figure 8 depicts this interaction. Except for treatments with 45% foliage, higher values were produced at 6 than at 10-min PT. In the case of bark, higher wood failure values were produced at 10-min PT which contradicts the shear strength test in which higher values were produced at 6-min PT.

In general, treatment with bark (UF-B30-10) gave the highest wood failure at 98%. The Duncan's test (Table 11) shows that, except for treatment UF-B45-6, the above result was not significantly different from the rest of the treatments. This indicates that bond quality in terms of wood failure was high for most treatments regardless of addition level. The lowest value (61%) was given by treatment UF-B45-6. It can be noted that shear strength and wood failure results are contradictory. As indicated earlier the relationship between shear strength and wood failure is not well defined and is still a subject of controversy.

The dry test provides a measure of initial bond strength. High initial bond strengths for the commercial resin were observed following addition of foliage or bark. This is important since UF resins are used for interior applications where durability (resistance to heat and moisture) may not be primordial. In terms of wood failure all treatments, except UF-B45-6, met the minimum 80% wood failure required by CSA Standards. The low wood failure value for treatment

UF-B45-6 can be explained by the high glue viscosity. As noticed during wood failure readings there was an evident lack of proper glue transfer between veneers. In terms of shear strength, with exception of two treatments, higher initial strengths were produced by foliage and bark mixes than with the control mix. From the above, the use of UF resin with foliage or bark appears advantageous when interior applications are contemplated.

5.4.2 Vacuum pressure-one cycle

Figure 3 and Table 5 show that treatments with foliage additions (UF-F15-10 and UF-F45 at 6 and 10-min PT) gave higher shear strengths than the control. Treatments with 30% foliage had similar values to the control. Treatments with bark additions UF-B30-6 and UF-B45-6 gave higher shear strength values than the control. Treatments with 15% foliage gave somewhat lower values than the control.

The ANOVA for the shear strength data (Table 8) shows the interaction M x PT highly significant. This interaction (Figure 9) implies that there was a different response among glue mixes to PT levels. PT did not appear to influence adhesion strength with UF-foliage treatments. Except for treatments with 15% foliage, similar values were produced at both PT levels. In the case of bark additions, PT appears to have influenced adhesive strength of

treatments with 30 and 45% additions. Higher values were produced at 6-min.

In general, treatments UF-B30-6, UF-B45-6 and UF-F15-10 produced the highest shear strengths at 1.94 MPa (281 psi), 1.92 MPa (279 psi) and 1.85 MPa (268 psi), respectively. In addition, Duncan's test (Table 13) shows that the above results are not significantly different at the 0.05 probability level. The lowest values were produced by treatments with 15% bark and those with 30% foliage.

Figure 3 and Table 5 also show that treatments with 30 and 45% foliage produced similar wood failure percentages to the control. Treatments with 15% additions gave slightly lower wood failure than 80%. Treatments with 15 and 30% bark produced similar values to the control which were higher than the minimum 80% required by CSA Standard.

The ANOVA for the wood failure data (Table 8) shows that the interaction M x PT is significant at the 0.05 level. Figure 9 depicts this interaction. As in the case of the dry test, PT did not seem to influence bond durability of UF-foliage treatments. Similar values were produced at both PT levels. In the case of bark additions, higher values were produced at 10-min PT. This indicates that with foliage additions the glue bonds attain a high degree of cure at 6-min while bark additions require higher energy. Chow (1972) has indicated that for plywood PF bonds, the

vacuum pressure test is more critical in detecting under-cured bonds than the dry, 24-hr cold soak and boil-dry-boil tests on the basis of wood failure evaluation. Furthermore, he emphasized that wood failure is a more sensitive measure of glue bond undercure than shear strength.

In general, the highest wood failure values were produced by treatments UF-C-6 (93%), UF-C-10 (89%); UF-F30-10(89%); UF-F45-6(87%), UF-F45-10(80%); UF-B15-6(83%), UF-B15-10(90%), UF-B30-6(85%) and UF-B30-10(90%). In addition, Duncan's test (Table 14) shows that these results are not significantly different at the 0.05 probability level. The lowest values were produced by UF-B45-6 (57%) and UF-B45-10 (70%) which were significantly lower than the other results.

As in the case of the dry test, results of shear strength and wood failure tests are contradictory. However, shear strength results from dry and vacuum pressure followed the same pattern. The UF-foliage treatments showed a slightly steady decrease in shear strength when submitted to vacuum pressure. The same occurred with UF-bark treatments, but there was not a significant decrease in shear strength in the cases of treatments with 30 and 45 % bark at 6-min PT.

Figures 2 and 3 show that wood failure percentage-dry and vacuum pressure-one cycle test data followed the same

pattern as above.

Among the UF-foliage treatments only 15% foliage addition gave significant decrease in bond quality. The same occurred with the UF-bark treatments, where only 45% bark addition showed a significant decrease in bond quality after the vacuum pressure cycle.

The wood failure percentage results indicate that with two exceptions (treatments with 15% foliage and 45% bark), treatments with foliage and bark additions exhibited good bond quality similar to the control. The slightly lower values given by treatments with 15% foliage may be due to veneer quality factors rather than glue properties, since mix formulation and properties were close to those of the control. These good results may be explained, in part, as due to the plasticizing action of water in reducing stress concentrations on the specimens glueline. It is also possible that additives such as wheat flour, foliage and bark enhance adhesion by better distributing stresses during exposure. The poor bond quality produced by mix with 45% bark can be explained by the high, unsuitable viscosity of this glue which did not allow proper spreading and transfer on the veneer surfaces.

5.4.3 Vacuum pressure-five cycles

Figure 4 and Table 5 show that treatments with low

foliage additions (UF-F15-6 and UF-F15-10) gave shear strengths higher than the control. Treatments UF-F30-6 and UF-F45-6 had somewhat lower values than the control. In the case of bark additions, treatment UF-B30-6 had higher shear strength than the control. Treatments UF-B30-10, UF-B45 at 6 and 10-min showed similar strengths to the control, while treatments with low bark additions (UF-B15-6 and UF-B15-10) produced the lowest values.

The ANOVA for the shear strength data (Table 9) indicates that the M and PT factors are highly significant. The interaction M x PT (Figure 10) was not significant implying that there was a similar response among treatments to PT levels. Except for treatment UF-B30-6, the results were higher for all treatments at 10-min PT.

In general, the highest shear strength values were produced by treatments UF-F15-10 (1.37 MPa, 199 psi), UF-F15-6 (1.34 MPa, 195 psi), UF-F45-10 (1.26 MPa, 183 psi); UF-B30-6 (1.49 MPa, 216 psi), UF-B30-10 (1.31 MPa, 190 psi) and the control UF-C-10 (1.35 MPa, 196 psi). In addition, Duncan's test (Table 13) indicates that these results are not significantly different at the 0.05 probability level. The lowest values were produced by treatments UF-F30-6 (0.90 MPa, 130 psi), UF-F45-6 (0.86 MPa, 124 psi); UF-B15-10 (0.95 MPa, 138 psi) and UF-B15-6 (0.70 MPa, 102 psi).

Figure 4 and Table 5 also show that treatment with 30% foliage gave similar wood failure percentage to the control at 10-min PT and lower at 6-min. Treatments with 15 and 45% foliage gave lower values than the control at both PT levels. In the case of bark additions, treatments with 15 and 30% bark gave slightly higher values than the control at 10-min PT and similar at 6-min. Treatment with 45% bark gave substantially lower wood failure percentage than the control.

The ANOVA for the wood failure percentage data (Table 9) shows that the M and PT factors are highly significant. The interaction M x PT (Figure 10) was not significant implying that there was a response among treatments to PT levels. The PT factor appeared to influence bond quality, all treatments produced higher values at 10-min PT. This suggests that stronger or more durable bonds are formed at longer PT and that co-reaction of UF resin with foliage or bark requires higher thermal energy to attain a high degree of cure.

In general, the highest wood failure values were produced by treatments UF-F30-10 (59%); UF-B15-10 (63%), UF-B30-10 (63%) and UF-C-10 (60%). Duncan's test (Table 14) indicates that these results are not significantly different at the 0.05 probability level. The lowest values were produced by treatments UF-F45-6 (15%) and UF-B45-6

(19%). It can be noted that large additions of either foliage or bark beyond 30% gave the lowest wood failure percentages.

The vacuum pressure-five cycles test is not included in the CSA Standards. It is a much more severe test than the vacuum pressure-one cycle, therefore, can provide a measure of bond degradation under more extreme conditions. Both, the veneer and the glue are submitted to severe stresses due to shrinking and swelling throughout the cycles. This treatment can be considered intermediate between vacuum pressure-one cycle and boil-dry-boil for evaluating bond durability.

It was noted while conducting the test that delaminations resulted after the second cycle with UF-F15-6 (5 delaminations) and UF-F45-6 (7 delaminations). After the third cycle, delaminations resulted in treatments UF-F15-6 (4), UF-F15-10 (3), UF-F45-6 (6) and UF-F45-10 (3). After the fourth cycle only UF-B45-6 showed delaminations (7). At the end of the fifth cycle the remaining specimens showed severe splits but were still suitable for shear testing. The above indicates that most delaminations occurred with foliage additions and that, as shown in Figure 4, stronger bonds were formed with bark additions. The results of UF-bark (15 and 30% additions) are in agreement with those of Hamada et al. (1969) who found

that cold soak bond strength of UF resins was increased by wattle bark addition.

5.4.4 Boil-dry-boil test

This test was conducted as specified by CSA Standards. All treatments, including the control delaminated completely in the first boiling cycle. This test was included on the assumption that UF resin modification with foliage and bark additions could improve bond durability to the point of resisting heat and moisture. The results indicate that no modifying improvements were made by these additions.

5.5 Modified Laboratory UF Glue (UFi) Properties

As shown in Table 4 mix with 30% foliage addition (UFi-F30) lowered viscosity below the control, while treatment with bark addition (UFi-B30) raised it above the control. As with the commercial UF resin, foliage addition to the mix resulted in decreased viscosity while bark tended to increase it. The lower viscosity of the UFi mix, compared with the standard UF, may be due to the relatively low viscosity of the UFi resin caused by its low molecular weight. Table 4 also shows that the pH and density values of UFi mixes were lower than of commercial UF mixes.

The gelation times were significantly shorter than those of UF mixes. This indicates that glue assembly time tolerance and pot life were reduced with UFi resin.

Mix stability as indicated by viscosity measurements decreased significantly after 24-hr. At such time only the mix with foliage addition remained workable. The mix with bark addition had too high viscosity and was unsuitable for spreading. After 48-hr all mixes were unworkable and viscosity measurements were not possible. Again, these results indicate the low stability of UFi mixes.

From the results it appears that both viscosity and stability were affected by the low molecular weight of the resin. As indicated by gelation time and stability tests the glue pot life was reduced considerably.

5.6 Bond Quality of Modified Laboratory UF Glue (UFi)

5.6.1 Dry test

As explained earlier, it is possible that a low molecular weight resin could provide a system with potential for reaction with foliage and bark low molecular weight phenolic compounds. To examine this a bond quality evaluation was made of UFi resin mixed with foliage and bark at the 30% addition level.

Figure 5 and Table 6 show that treatments with 30% foliage gave higher shear strength values than the control while treatments with bark gave similar values to the control.

The ANOVA for the shear strength data (Table 10) shows the main factor glue mix (M) as highly significant. The interaction M x PT (Figure 11) was not significant, implying that there was a response among treatments to PT levels. All treatments including the control, produced higher shear values at 6-min PT. Treatments UFi-30 at 6 and 10-min PT gave the highest values of 1.6 MPa (232 psi) and 1.54 MPa (223 psi), respectively. Duncan's test (Table 15) shows these results as not significantly different at the 0.05 level and that they are significantly different than those of the control and bark treatments. The lowest value of 1.22 MPa (177 psi) was given by the control mix.

In general, shear strength data were relatively low indicating that the initial bond strength was reduced when the low molecular weight resin was used.

In terms of wood failure percentage, Figure 5 shows that treatments with bark addition gave the highest values while foliage additions gave similar values to the control.

The ANOVA for the wood failure percentage data shows the main M and PT factors as highly significant. The interaction M x PT was not significant. As with the shear strength test, there was a response among treatments to PT levels. Higher results were produced at 6-min PT. The highest wood failure values were given by treatments UFi-B30-6 (93%) and UFi-F30-6 (89%). Duncan's test shows these results as not significantly different from those produced by UFi-C-6 (82%) and UFi-B30-10 (86%). All treatments, with exception of UFi-C-10 (72%) and UFi-F30-10 (78%) met the minimum CSA bond quality requirements.

The overall results of this test are lower than those produced by the commercial UF treatments at equivalent addition levels. As indicated earlier, an explanation for decreased initial bond quality with UFi resin treatments would be the lower cohesive strength of this resin resulting from its smaller initial molecular size. However, it should be noted that better results were obtained with bark and foliage than with the control. This suggests that some

degree of reaction between the resin and foliage or bark was attained.

5.6.2 Vacuum pressure-one cycle

Figure 6 and Table 6 show that treatments with foliage and bark produced higher shear strength values than the control.

The ANOVA for the shear strength data (Table 11) shows the M and PT factors as highly significant. The interaction M x PT (Figure 12) was not significant which indicates similar responses among treatments to PT levels. Higher results were produced at 10-min PT. The highest shear strength result was given by treatment UFi-B30-10 (1.37 MPa, 199 psi). Duncan's test (Table 16) shows this result as significantly different than those of the other treatments. The lowest values were given by the control treatments UFi-C-6 (0.92 MPa, 134 psi) and UFi-C-10 (1.01 MPa, 147 psi).

In terms of wood failure percentage, Figure 6 also shows that the highest values were produced by treatments UFi-F30-6 (86%), UFi-F30-10 (87%) and UFi-B30-6 (92%). Duncan's test shows these results as significantly higher than those of the control. The lowest values were given by the controls UF-C-6 (59%) and UF-C-10 (66%).

The ANOVA for the wood failure percentage data shows the interaction M x PT (Figure 12) as not significant.

Treatments with foliage and the control gave higher values at 6-min PT while those with bark gave similar values at both PT levels.

Following vacuum pressure-one cycle bond quality in terms of shear strength decreased substantially for treatments with foliage and the control. In terms of wood failure, foliage and bark additions gave higher bond quality than the control. This suggests that foliage and bark components take up residual formaldehyde and react with the resin resulting in improved adhesion.

5.6.3 Vacuum pressure-five cycles

Figure 7 and Table 6 show that treatments with bark gave higher shear strength values than the control while foliage additions(at 6-min PT) gave the lowest values. The ANOVA for the shear strength data (Table 13) shows the interaction M x PT as highly significant. This interaction, shown in Figure 13, indicates a different response among treatments to PT levels.

The highest shear strength values were produced by treatments UFi-B30-6 (0.56 MPa, 81 psi) and UFi-B30-10 (0.61 MPa, 84 psi) which are not significantly different at the 0.05 level. The lowest value of 0.40 MPa (58 psi) was given by UFi-F30-6.

The ANOVA for wood failure percentage data (Table 14)

shows the interaction $M \times PT$ as significant which indicates a different response among treatments to PT levels (Figure 13). As shown in Figure 7 the highest wood failure percentage was produced by treatment UF-F30-10 (36%) which is not significantly different from those of treatments UFi-C-10 (20%) and UF-B30-6 (20%). Treatment UFi-B30-10 gave the lowest value at 9%.

In general, all treatments produced low results. An examination of ruptured shear specimens showed glue hydrolysis. It appears clear that the low molecular weight glue had lower cohesive strength as result of its low degree of polymerization. Cohesive forces are generally high in commercial synthetic resins. Also, it has been pointed out earlier that viscosity is a function of molecular weight. Low molecular weight glues usually give low viscosity which may cause undesirable glue overpenetration into the veneer affecting bond quality. Conversely, high molecular weight glues generally give high viscosity which affects glue flow and transfer on veneer surfaces resulting in decreased adhesion. Consequently, a glue should have a proper molecular weight distribution to produce a high cohesive strength and suitable viscosity which in turn develops strong wood-glue bonds.

The boil-dry-boil test as in the case of the commercial UF glue resulted in complete delamination of test specimens.

5.7 Use of Foliage and Bark with UF Resins

Results from bond quality evaluation indicated that foliage and bark action as modifiers is limited. No UF mix survived boiling treatment, which implies that exterior glueline durability can not be achieved by these modifications. Because of this result the vacuum pressure-five cycle became the critical test for evaluating bond durability. In this case formulations with the commercial UF resin and bark(15 and 30%) yielded 3 to 12% higher wood failure than the control, while 30% foliage gave similar results to the control. This indicates that under accelerated aging conditions durability was not substantially improved. Conversely, following dry and vacuum pressure-one cycle treatments, most formulations containing foliage and bark yielded high bond quality (above 80% wood failure). This clearly indicates that UF resin bond quality is well maintained by foliage and bark additions even when exposed to high moisture conditions.

From the above, it appears evident that foliage and bark action follows that of glue extenders rather than of modifiers. As indicated earlier, a modifier involves glue bond durability improvement, while an extender is added to improve the adhesive action of the glue mix. Extenders improve viscosity control and pot life, reduce dry-out and facilitate spread of active glue solids on a specific surface area.

Special wheat flours possess ideal properties for use as UF extenders which includes inherent adhesiveness, fine particle size, uniformity, and low ash content. Some physical tests conducted in this study demonstrated that foliage and bark impart good properties to UF glues similar to those mentioned above. In addition, in the case of foliage, it was found that this material was effective in maintaining glue stability, viscosity increased more slowly over a 48-hr period. The inherent adhesiveness of foliage has been proven already by Chow, Steiner and Rozon (1979) who reported that foliage alone without addition of synthetic resin can develop strong adhesive properties.

Bark also has important properties and has been used as a filler for phenolic glues for a long time. Bark is especially attractive for its high phenolic content (30 to 70%) which are highly reactive components. Special attention has been given for a long time to the use of bark extractives as wood adhesives. The feasibility of using formaldehyde and various bark extracts to bond plywood and particleboard has been demonstrated (Hall et al., 1970; Anderson et al., 1974; Steiner and Chow, 1975). In this study bark addition to UF resin increased reactivity and slightly improved bond durability under cyclical testing.

The above indicates that foliage and bark have good properties and can be used successfully as part of the

extender system in UF formulations. As mentioned earlier both materials can substitute for wheat flour up to 40% (extender weight basis) without affecting glue mix properties. In addition, use of these materials includes other benefits, such as: 1) More complete tree utilization; 2) Use of largely unused, non-food materials; 3) Simple processing for use as extenders involving raw material collection, drying and grinding; and 4) Use of extenders made from local materials is important, especially for countries where imported wheat flour and resin costs are a great burden.

6.0 CONCLUSIONS

- 1) Untreated white spruce foliage and western hemlock bark powders exhibited physical properties compatible with UF glues. Both materials were easily pulverized to fine particle-size when dried to moisture contents below 10%. These foliage and bark are acidic (pH 4.3 and 4.7, respectively) and ash contents were relatively low (3.7 and 2.3%).
- 2) UF glue modification with foliage to 30% level (based on resin solids) gave lower viscosity than the conventional wheat flour extended UF glue. Conversely, bark addition to the same level increased viscosity. These viscosities, however, were all within suitable limits and did not affect glue workability significantly. Foliage and bark additions at 45% levels, however, increased viscosity to a point that affected glue flow, spreadability and pot life.

The laboratory UF glue modified with 30% foliage and bark gave lower viscosity than the modified commercial UF glue mixes. Glue density and pH decreased with foliage and bark additions and were lower than those of the control. Foliage additions gave similar gelation times as the control whereas, bark shortened times. The modified laboratory UF glue gave significantly

shorter gelation times than the modified commercial UF mixes. UF mix stability, as indicated by viscosity tests after one, 24 and 48-hr was best maintained by foliage addition to a 30% level. Stability of mixes with bark additions to a 30% level was similar to the control. Higher foliage and bark addition levels decreased mix stability and after 48-hr were unworkable.

- 3) DSC analyses examining the influence of foliage and bark on UF glue curing properties showed a slight increase of exothermic peak temperature when these materials were added to a UF mix. This effect may relate to improved assembly time tolerance and glue pot life.
- 4) Treatments bonded with the commercial UF glue produced higher shear strength and wood failure percentage results than treatments bonded with the laboratory glue.
- 5) Treatments bonded with the commercial glue produced high initial shear strength and wood failure percentage in the dry test. Bond quality in terms of wood failure percentage was highest for treatment with 30% foliage at 6-min PT, and treatments with 15 and 30% bark at 10-min PT.

The vacuum pressure-one cycle did not reduce bond quality significantly. In terms of wood failure

percentage treatments with 30% foliage and 15 and 30% bark produced the highest bond quality, similar to the control.

Following vacuum pressure-5 cycles bond strength was reduced significantly. In terms of wood failure, treatments with 15 and 30% bark had slightly higher bond quality than the control; treatment with 30% foliage at 10 min PT had similar bond quality to the control. Influence of the PT factor became evident in this test as bond quality was best at 10-min PT for all treatments.

- 6) The boil-dry-boil test used to assess durability improvement of UF glue by modification with foliage and bark resulted in complete delamination. This result indicates that no improvement to the usual poor performance under heat and moisture conditions accompanied these modifications.
- 7) Dried and pulverized foliage and bark were used successfully to replace up to 40% of the conventional wheat flour extender.

LITERATURE CITED

- Anderson, A.B., Wong, A. and K-T. Wu. 1974. Utilization of white fir bark in particleboard. Forest Prod. J. 24(1): 51-54.
- American Society for Testing Materials. 1978. Annual book of ASTM standards. Part 22. Wood; Adhesives. Philadelphia. 1062 pp.
- Bauer, H.H., Christian, G.D. and J.E. O'Reilly. 1978. Instrumental Analysis. Allyn and Bacon, Inc. Boston. 832 pp.
- Barton, G.M., McIntosh, J.A. and S. Chow. 1978. The present status of foliage utilization. Reprint from AICHE Symposium Series No. 177. 74: 124-131.
- Blomquist, R.F. and W.Z. Olson. 1957. Durability of urea-resin glues at elevated temperatures. Forest Prod. J. 7(8): 266-272.
-
- _____. 1964. Durability of urea-resin glues exposed to exterior weathering. Forest Prod. J. 14(10): 461-466.
- Brown, H.P., Panshin, A.J. and C.C. Forsaith. 1952. Textbook of Wood Technology. Vol. II. Mac Graw-Hill Book Co., New York. pp. 185-208.

Canadian Standards Association. 1977. Wood adhesives.

CSA 0112M-1977. Rexdale, Ont. 104 pp.

_____. 1978. Douglas-fir plywood.

CSA 0121M-1978. Rexdale, Ont. 37 pp.

Chow, S. 1974. Lathe-check influence on plywood shear strength. Information Report VP-X-122. Dept. of the Environment, Can. Forest Serv., Western For. Prod. Lab., Vancouver. 13 pp.

_____. 1975. Bark boards without synthetic resins. Forest Prod. J. 25(11): 32-37.

_____. 1977. Foliage as adhesive extender: A progress report. Symposium on Particleboard. Pullman, Washington. pp. 89-98.

_____ and K.S. Chunsi. 1979. Adhesion strength and wood failure relationship in wood-glue bonds. J. Japan Wood Res. Soc. 25(2): 125-131.

_____ and W.V. Hancock. 1969. Method for determining degree of cure of phenolic resin. Forest Prod. J. 19(4): 21-29.

_____ and P.R. Steiner. 1975. Catalytic, exothermic reactions of UF resin. Holzforsch. 29: 5-10.

_____. 1979. Comparison of the cure of PF novolac and resol systems by DSC. J. Appl. Polymer Sci. 23: 1973-1985.

Chow, S., Steiner, P.R. and L. Rozon. 1979. Efficiency of coniferous foliage as extenders for powdered phenolic resin. 13th Particleboard Symposium. Pullman, Washington. pp. 329-342.

_____ and G E. Troughton. 1975. Thermal reactions of phenol-formaldehyde resins in relation to molar ratio and bond quality. Wood Science 8(1): 343-349.

_____, Troughton, G.E., Hancock, W.V. and H.N. Mukai. 1973. Quality control in veneer drying and plywood gluing. Information Report VP-X-113. Dept. of the Environment, Can. Forest Serv., Western For. Prod. Lab., Vancouver. 33 pp.

_____ and W.G. Warren. 1972. Efficiency of plywood bond-quality testing methods. Information Report VP-X-104. Dept. of the Environment, Can. Forest

Driehuyzen, H.W. and R.W. Wellwood. 1960. Effect of temperature and humidity of glue room on open assembly time. Forest Prod. J. 10(5): 254-259.

Fisher, C. and D.W. Benseid. 1969. Gluing of southern pine veneer with blood modified phenolic resin glues. Forest Prod. J. 19(5): 32-37.

Gillepsie, R.H., Olson, W.Z. and R.F. Blomquist. 1964.

Durability of urea-resin glues modified with polyvinyl acetate and blood. Forest Prod. J. 14(8): 343-349.

Hall, R.B., Leonard, J.H. and G.A. Nicholls. 1960.

Bonding particleboard with bark extracts. Forest Prod. J. 10(5): 243-272.

Hamada, R., Ikeda, S. and Y. Satake. 1969. Utilization

of wood bark for plywood adhesive. II. J. Japan Wood Res. Soc. 15(8): 171-175.

Hancock, W.V. 1980. Veneer Roughness. Forintek Corp.

Western For. Prod. Lab., Vancouver. Private communication.

Herrick, F.W. and L.H. Bock. 1958. Thermosetting exterior

plywood type adhesives from bark extracts. Forest Prod. J. 8: 269-274.

Hill, R. 1952. Urea and melamine adhesives. J. Forest

Prod. Res. Soc. 2(3): 104-116.

Hirata, S. and N. Mineura. 1974. The utilization of

starch wastes as a filler for adhesives. J.

Hokkaido Forest Prod. Res. Inst. 22(7): 10-14.

- Imura, S., Sato, M., Nakamura, H. and I. Abe. 1974.
Effects of bark on the adhesive strength of UF
resin. J. Hokkaido Forest Prod. Res. Inst.
23(3): 10-14.
- Kennedy, E.I. 1965. Strength and related properties of
wood grown in Canada. Publ. 1104. Can. Dept.
Forestry. 51 pp.
- Klein, J.A. 1975. Chemical aspects of gluing plywood
with phenolic resins. FPRS Meeting, Portland.
7 pp.
- Knudson, R.M., Stout, R.M.T. and Rogerson, D.E. 1978.
Plywood glue extender from particleboard sander-
dust. Forest Prod. J. 28(9): 44.
- Kollmann, F.F.P., Kuensi, E.W. and A.J. Stamm. 1975.
Principles of Wood Science and Technology. II.
Wood Based Materials. Springer Verlag, New York.
703 pp.
- Kubota, M. and M. Saito. 1974. The utilization of saw-
dust as filler for plywood adhesives. J. Hokkaido
Forest Prod. Res. Inst. 23(8): 5-9.
- McLean, H. and J.A.F. Gardner. 1952. Bark extracts in
adhesives. Pulp Paper Mag. Can. 53(8): 111-114.

- Marra, G.G. 1964. Functional components of wood adhesion. Proceedings of the conference on theory of wood adhesion. U. Michigan, Ann Arbor. 1:3:1.
- Marian, J.E. and D.A. Stumbo. 1962. Adhesion in wood. I. Physical factors. Holzforsch. 16:134-148.
- _____ and C.W. Maxey. 1958. Surface texture of wood as related to glue-joint strength. Forest Prod. J. 8(12): 345-351.
- Meyer, B. 1979. Urea formaldehyde resins. Addison-Wesley Pub. Co., London. 423 pp.
- Northcott, P.L. 1952. The development of the glue-line-cleavage test. J. Forest Prod. Res. Soc. 2(5): 216-224.
- _____. 1955. Bond strength as indicated by wood failure or mechanical test. Forest Prod. J. 5(2): 118-123.
- _____, Colbeck, H.G.M., Hancock, W.V. and K.C. Shen. 1959. Undercure: casehardening in plywood. Forest Prod. J. 9(12): 442-451.
- _____ and D.C. Walser. 1965. Veneer-roughness scale. B.C. Lumberman 7:80-82.

- Palka, L.C. 1964. Factors influencing the strength properties of Douglas fir plywood normal to glue-line. Unpubl. MF thesis, Dept. of Forestry, The University of B.C., 73 pp.
- Parkes, R.S.R. and P. Taylor. 1966. Adhesion and Adhesives. Pergamon Press, Oxford. 142 pp.
- Rayner, C.A.A. 1965. Synthetic organic adhesives. Adhesion and Adhesives, Vol. I. Elsevier Pub. Co., New York. pp. 187-337.
- Ramos Garcia, J.M. 1965. Bleedthrough of adhesive in tropical hardwood plywood. Unpubl. MF thesis. University of Washington, Seattle. 93 pp.
- Rice, J.F. 1965. The effect of urea formaldehyde resin viscosity on plywood bond durability. Forest Prod. J. 15(3): 107-112.
- Robertson, J.E. 1966. Let's analyze the glue extender problem. Plywood and Panel 7(1): 30.
- _____. 1974. Plant-site observations of Asian plywood glue extenders. Forest Prod. J. 24(11): 35-41.
- _____ and R.R. Robertson. 1979. Fillers and extenders in plywood production: U.S. and Foreign practices. Forest Prod. J. 29(6): 15-21.

- Rosales, D.A. 1980. Comparison of plywood manufacture in Peru and the interior of British Columbia. Unpubl. FRST 580 report. Dept. of Forestry, The University of B.C., 51 pp.
- Rose, A. 1957. Chemical control of hot press UF glue mixes. Forest Prod. J. 7(11): 30A-33A.
- Sellers, T. 1976. A plywood review and its chemical implications. Symposium on chemical aspects of solid wood and board technology. Reichhold chemicals, Inc., Tuscalosa. pp. 11-14.
- Shen, K.C. 1958. The effect of dryer temperature, sapwood and heartwood, and time elapsing between drying and gluing on the gluing properties of Engelmann spruce veneer. Unpubl. MF thesis, Dept. of Forestry, The University of B.C., 36 pp.
- Shields, J. 1975. Adhesives Handbook. SIRA. Ministry of technology, Ohio. 355 pp.
- Scott, D.S. 1956. Recovery of tannins from western hemlock bark. I. Extraction rates with water as solvent. Pulp Paper Mag. Can. 57(4): 139-141.
- Steiner, P.R. 1973. Durability of urea formaldehyde adhesives: Effects of molar ratio, second urea, and filler. Forest Prod. J. 23(12): 32-38.

Steiner, P.R. 1980. Foliage and bark water uptake.

Forintek Corp., Western Forest. Prod. Lab.,
Vancouver. Personal communication.

_____ and S. Chow. 1974. Comparison of modifiers
for durability improvement of urea-formaldehyde
resin. Wood and Fiber 6(1):57-65.

_____. 1975. Factors influencing
western hemlock bark use as adhesives. Information
Report VP-X-153. Dept. of the Environment, Can.
Forest Serv., Western For. Prod. Lab., Vancouver.
13 pp.

Stone, M.D. and P. Robitscheck. 1978. Factors affecting
the performance of plywood glue extenders. Forest
Prod. J. 28(6):32-35.

Strickler, M.D. and E.W. Sawyer. 1974. Attapulgitic clay-
a filler for exterior plywood adhesives. Forest
Prod. J. 24(11): 17-22.

Stumbo, D.A. 1964. Influence of surface aging prior to
gluing on bond strength of Douglas-fir and red-
wood. Forest Prod. J. 23(12): 32-38.

Thomas, R.J. and F.W. Taylor. 1962. Urea formaldehyde
resins modified with water-soluble blood. Forest
Prod. J. 13(3): 111-115.

Troughton, G.E. 1968. Accelerated aging of glue-wood bonds. Wood Science 1: 172-176.

Truax, T.R. 1929. The gluing of wood. Bul. 1500.
U.S.D.A., 23 pp.

Yavorski, J.M., Cunningham, J.H., and N.G. Hundley. 1955.
Survey of factors affecting strength tests of
glue joints. Forest Prod. J. 5: 306-311.

Zisman, W.A. 1963. Influence of constitution on adhesion.
I. & E.C. 55(10): 19-38.

Table 1. Veneer quality analyses.
(3.17 mm Douglas-fir veneer)

	Mean	SD [*]	Max	Min	Range
1. Roughness (n=50) (mm)	0.33	0.08	0.51	0.13	0.38
2. Thickness (n=50) (mm)	3.20	0.04	3.27	3.09	0.18
3. Moisture content (n=50) (%)	6.6	0.6	7.8	5.3	2.5
4. Lathe-check depth ^{**} (n=50) (%)	75	10	90	60	30
5. Lathe-check angle ^{**} (n=50) (deg.)	60	5	70	50	20

* Standard deviation

** Measured from three longest lathe-checks

Table 2. Veneer roughness measurements (n=50).

Roughness Scale	mm; equivalent	Frequency number	Frequency (%)
0	0.00	0	0.0
1	0.13	3	6.0
2	0.25	16	32.0
3	0.38	30	60.0
4	0.51	$\frac{1}{50}$	$\frac{2.0}{100.0}$

Table 3. Foliage and Bark powder properties.

	Moisture content (n=2)	Moisture content (%)	Ash content* (%)	pH(n=2)
White spruce foliage	6.2		3.7	4.3
Western hemlock bark	8.0		2.3	4.7

Particle size distribution
(%)

White spruce foliage (n=2)

<u>Particle sizes</u>	weight (%)
Retained on 100 mesh	3.4
Retained on 200 mesh	14.8
Retained on 325 mesh	40.6
Smaller than 325 mesh	41.2

Western hemlock bark (n=2)

Retained on 100 mesh	3.9
Retained on 200 mesh	17.8
Retained on 325 mesh	34.8
Smaller than 325 mesh	43.5

* Data obtained from Forintek Canada Corp.

Table 4. Glue mix physical properties.

Glue mix	Viscosity [*] (cps)			pH [*]	Density [*] (g/cc)	Gelation Time(min)
	1 hr	24-hr	48-hr			
UF-C	5,100	9,700	12,800	6.4	1.14	23.0
UF-F15	4,600	7,900	10,500	5.7	1.11	23.5
UF-F30	4,300	7,100	9,250	5.6	0.96	23.5
UF-F45	5,600	----- ^{**}	----- ^{**}	5.3	0.98	25.5
UF-B15	6,200	9,750	10,900	6.1	1.08	20.0
UF-B30	7,200	10,300	----- ^{**}	5.9	1.06	21.0
UF-B45	7,800	----- ^{**}	----- ^{**}	5.2	1.03	17.0
<hr/>						
UFi-C	4,400	11,600	----- ^{**}	6.1	1.10	10.0
UFi-F30	3,900	9,400	----- ^{**}	5.3	0.92	11.0
UFi-B30	4,700	12,400	----- ^{**}	5.5	1.02	8.0

^{*} Measured without NH_4Cl catalyst.

^{**} Glues developed too high viscosity to record on viscometer scale ($> 20,000$ cps).

Table 5. Average (n=20) shear strengths and wood failure percentages of UF glue treatment combinations.

Treatments	DRY TEST		VACUUM PRESSURE TEST		VACUUM PRESSURE-5 CYCLES	
	Mean Shear Strength (psi)	Mean Wood Failure (%)	Mean Shear Strength (psi)	Mean Wood Failure (%)	Mean Shear Strength (psi)	Mean Wood Failure (%)
UF-C-6	214	92	199	93	152	51
UF-C-10	238	91	225	89	196	60
UF-F15-6	225	89	208	79	195	19
UF-F15-10	302	85	268	78	199	39
UF-F30-6	244	95	195	88	130	24
UF-F30-10	242	91	194	89	152	59
UF-F45-6	269	81	241	87	124	15
UF-F45-10	268	90	240	80	183	33
UF-B15-6	232	88	190	83	102	47
UF-B15-10	217	96	185	90	138	63
UF-B30-6	283	95	281	85	216	44
UF-B30-10	265	98	226	90	190	63
UF-B45-6	293	61	279	57	158	19
UF-B45-10	263	87	222	70	169	29

Note: 1. Figures rounded to the nearest unit.
2. Treatment codes are shown in Appendix II.

Table 6. Average (n=20) shear strengths and wood failure percentages of UFi* glue treatment combinations.

Treatments	DRY TEST		VACUUM PRESSURE TEST		VACUUM PRESSURE-5 CYCLES	
	Mean Shear Strength (psi)	Mean Wood Failure (%)	Mean Shear Strength (psi)	Mean Wood Failure (%)	Mean Shear Strength (psi)	Mean Wood Failure (%)
UFi-C-6	196	82	134	66	79	18
UFi-C-10	177	72	147	59	77	20
UFi-F30-6	232	89	178	86	58	18
UFi-F30-10	223	78	179	87	92	36
UFi-B30-6	196	93	174	92	81	20
UFi-B30-10	194	86	199	78	84	9

*UFi, Low molecular weight UF resin.

Note: 1. Figures rounded to the nearest unit.
2. Treatment codes are shown in Appendix II.

Table 7. Analysis of variance for dry-shear strengths and wood failure percentages for testing the effect of glue mix and pressing time on the UF-glue bond quality.

Shear Strength				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	6	0.12198x10 ⁶	20330.0	30.10**
Pressing time(PT)	1	1555.7	1555.7	2.30
Panel (P)	1	488.93	488.93	0.72
MxPT	6	78629.0	13105.0	19.40**
PTxP	1	300.36	300.36	0.44
MxP	6	16931.0	2821.8	4.18**
MxPTxP	6	37590.0	6264.9	9.28**
Residual	252	0.17020x10 ⁶	675.42	
Total	279	0.42768x10 ⁶		

Wood Failure				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	6	13010.0	2168.4	10.48**
Pressing time(PT)	1	1966.3	1966.3	9.51**
Panel (P)	1	276.01	276.01	1.33
MxPT	6	6692.3	1115.4	5.39**
PTxP	1	565.73	565.73	2.73
MxP	6	5123.6	853.93	4.13**
MxPTxP	6	2848.9	474.81	2.30**
Residual	252	52104.0	206.76	
Total	279	82587.0		

* Significant at the 0.05 level.

** Significant at the 0.01 level.

Table 8. Analysis of variance for vacuum pressure-shear strengths and wood failure percentages for testing the effect of glue mix and pressing time on the UF glue bond quality.

Shear Strength				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	6	0.17729x10 ⁶	29549.0	29.09**
Pressing time(PT)	1	1462.9	1462.9	1.44
Panel (P)	1	8803.2	8803.2	8.66**
MxPT	6	0.10504x10 ⁶	17507.0	17.23**
PTxP	1	300.36	300.36	0.30
MxP	6	21182.0	3530.3	3.47**
MxPTxP	6	83720.0	13953.0	13.73**
Residual	252	0.25597x10 ⁶	1015.8	
Total	279			

Wood Failure				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	6	20929.0	3488.1	16.25**
Pressing time(PT)	1	260.36	260.36	1.21
Panel (P)	1	38.629	38.629	0.18
MxPT	6	3228.9	538.16	2.50*
PTxP	1	660.36	660.36	3.07
MxP	6	5502.9	917.15	4.27**
MxPTxP	6	6110.3	1018.4	4.74**
Residual	252	54075.0	214.58	
Total	279	90805.0		

* Significant at the 0.05 level.

** Significant at the 0.01 level.

Table 9. Analysis of variance for vacuum pressure five cycle-shear strengths and wood failure percentages for testing the effect of glue mix and pressing time on the UF glue bond quality.

Shear Strength				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	6	0.21257×10^6	35428.0	8.22**
Pressing time(PT)	1	32342.0	32342.0	7.51**
Panel (P)	1	211.04	211.04	0.48×10^{-1}
MxPT	6	48449.0	8074.8	1.87
PTxP	1	4204.7	4204.7	0.97
MxP	6	0.20018×10^6	33364.0	7.74**
MxPTxP	6	60050.0	10008.0	2.32*
Residual	252	0.10859×10^6	4309.0	
Total	279	0.16438×10^6		

Wood Failure				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	6	51447.0	8574.6	13.66**
Pressing time(PT)	1	23461.0	23461.0	37.39**
Panel (P)	1	10.032	10.032	0.15×10^{-1}
MxPT	6	746.81	746.81	1.19
PTxP	1	1449.2	1449.2	2.31
MxP	6	14618.0	2436.3	3.88**
MxPTxP	6	14959.0	2493.2	3.97**
Residual	252	0.15808×10^6	627.3	
Total	279	0.26851×10^6		

*Significant at the 0.05 level

**Significant at the 0.01 level

Table 10. Analysis of variance for dry-shear strengths and wood failure percentages for testing the effect of glue mix and pressing time on the UFi glue bond quality.

Shear Strength				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	2	36487.0	18243.0	22.06**
Pressing time(PT)	1	2900.8	2900.8	3.50
Panel (P)	1	7.5	7.5	0.90x10 ⁻²
MxPT	2	1541.7	770.83	0.93
PTxP	1	607.5	607.5	0.73
MxP	2	845.0	422.5	0.51
MxPTxP	2	605.0	302.5	0.36
Residual	108	89315.0	826.99	
Total	119	0.13231x10 ⁶		

Wood Failure				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	2	3227.8	1613.9	4.84**
Pressing time(PT)	1	2585.4	2585.4	7.76**
Panel (P)	1	106.41	106.41	0.31
MxPT	2	115.82	57.908	0.17
PTxP	1	57.408	57.408	0.17
MxP	2	256.32	128.16	0.38
MxPTxP	2	816.32	408.16	1.22
Residual	108	35962.0	332.98	
Total	119	43128		

* Significant at the 0.05 level.

** Significant at the 0.01 level.

Table 11. Analysis of variance for vacuum pressure-shear strengths and wood failure percentages for testing the effect of glue mix and pressing time on the UFi glue bond quality.

Shear Strength				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	2	48701.0	24351.0	43.73**
Pressing time(PT)	1	5005.2	5005.2	8.98**
Panel (P)	1	1300.2	1300.2	2.33
MxPT	2	2587.9	1294.0	2.32
PTxP	1	16.875	16.875	0.30x10 ⁻¹
MxP	2	2240.4	1120.2	2.01
MxPTxP	2	908.75	454.37	0.81
Residual	108	60137.0	556.83	
Total	119	0.12090x10 ⁶		

Wood Failure				
Glue mix (M)	2	14382.0	7190.9	16.50**
Pressing time(PT)	1	1280.5	1280.5	2.93
Panel (P)	1	5.633	5.633	0.12x10 ⁻¹
MxPT	2	1022.5	511.23	1.17
PTxP	1	554.70	554.70	1.27
MxP	2	67.267	33.63	0.77x10 ⁻¹
MxPTxP	2	178.40	89.20	0.20
Residual	108	47051.0	435.66	
Total	119	64542		

* Significant at the 0.05 level.

** Significant at the 0.01 level.

Table 12. Analysis of variance for vacuum pressure five cycle-shear strengths and wood failure percentages for testing the effect of glue mix and pressing time on the UFi glue bond quality.

Shear Strength				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	2	1096.3	548.13	1.32
Pressing time(PT)	1	3910.2	1910.2	9.41**
Panel (P)	1	1300.2	1300.2	3.13
MxPT	2	7632.9	3816.5	9.19**
PTxP	1	200.21	2700.2	0.48
MxP	2	5400.4	2700.2	6.50**
MxPTxP	2	3100.4	1550.2	3.73
Residual	108	44857.0	415.35	
Total	119	67498.0		

Wood Failure				
Source	Degrees of Freedom	Sum of Square	Mean Square	F Ratios
Glue mix (M)	2	2930.4	1465.2	2.40
Pressing time(PT)	1	226.88	226.88	0.37
Panel (P)	1	75.208	75.208	0.12
MxPT	2	4366.2	2183.1	3.58*
PTxP	1	91.875	91.875	0.15
MxP	2	125.42	62.708	0.10
MxPTxP	2	11.25	5.625	0.92x10 ⁻²
Residual	108	65837.0	609.61	
Total	119	73665.0		

* Significant at the 0.05 level.

** Significant at the 0.01 level.

Table 13. Duncan's multiple range tests for shear strengths of treatments bonded with UF glue.

T R E A T M E N T					R A N K I N G *									
Dry Test	1	10	3	9	2	6	5	14	12	8	7	11	13	4
Treatment **	214	217	225	232	238	242	244	263	265	268	269	283	293	302
Mean	_____				_____			_____		_____			_____	

Vacuum Pressure test

Treatment	10	9	5	6	1	3	14	2	12	8	7	4	13	11
Mean	185	190	194	194	199	208	222	225	226	240	241	268	279	281

Vacuum Pressure-5 Cycles test

	9	7	5	10	6	1	13	14	8	12	3	2	4	11
Treatment**	102	124	130	138	152	152	158	169	183	190	195	196	199	216
Mean	_____				_____					_____			_____	

* Means underscored by the same line are not significantly different at the 5% level of significance.

**Means above refer to treatments as follows:

1	UF-C-6	5	UF-F30-6	9	UF-B15-6	13	UF-B45-6
2	UF-C-10	6	UF-F30-10	10	UF-B15-10	14	UF-B45-10
3	UF-F15-6	7	UF-F45-6	11	UF-B30-6		
4	UF-F15-10	8	UF-F45-10	12	UF-B30-10		

Table 14. Duncan's multiple range tests for wood failure percentages of treatments bonded with UF glue.

T R E A T M E N T R A N K I N G *															
<u>Dry Test</u>															
Treatment	**	13	7	4	14	9	3	8	2	6	1	5	11	10	12
Mean		61	81	85	87	88	89	90	91	91	92	95	95	96	98
<div><div>—</div><div><div></div><div></div><div></div><div></div></div></div>															
<u>Vacuum Pressure Test</u>															
Treatment	**	13	14	4	3	8	9	11	7	5	2	6	12	10	1
Mean		57	70	78	79	80	83	85	87	88	89	89	90	90	93
<div><div>—</div><div><div></div><div></div><div></div><div></div></div></div>															
<u>Vacuum Pressure-5 Cycles Test</u>															
Treatment	**	7	13	3	5	14	8	4	11	9	1	6	2	10	12
Mean		15	19	19	24	29	33	39	44	47	51	59	60	63	63
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* Means underscored by the same line are not significantly different at the 5% level of significance.

** Means above refer to treatments as follows:

1	UF-C-6	5	UF-F30-6	9	UF-B15-6	13	UF-B45-6
2	UF-C-10	6	UF-F30-10	10	UF-B15-10	14	UF-B45-10
3	UF-F15-6	7	UF-F45-6	11	UF-B30-6		
4	UF-F15-10	8	UF-F45-10	12	UF-B30-10		

Table 15. Duncan's multiple range tests for shear strengths of treatments bonded with UFi glue.

	T R E A T M E N T			R A N K I N G *		
<u>Dry Test</u>	2	6	5	1	4	3
Treatment Mean **	177	194	196	196	223	232
<hr/>						
<u>Vacuum Pressure Test</u>	1	2	5	3	4	6
Treatment Mean **	134	147	174	178	179	199
<hr/>						
<u>Vacuum Pressure-5 Cycles Test</u>	3	2	1	5	6	4
Treatment Mean **	58	77	79	81	84	92
<hr/>						

* Means underscored by the same line are not significantly different at the 5% level of significance.

** Means above refer to treatments as follows:

1. UFi-C-6
2. UFi-C-10
3. UFi-F30-6
4. UFi-F30-10
5. UFi-B30-6
6. UFi-B30-10

Table 16. Duncan's multiple range test for wood failure percentages of treatments bonded with UFi glue.

T R E A T M E N T R A N K I N G *						
<u>Dry Test</u>	2	4	1	6	3	5
Treatment Mean **	72	78	82	86	89	93
<hr/>						
<u>Vacuum Pressure Test</u>	2	1	6	3	4	5
Treatment Mean **	66	59	78	86	87	92
<hr/>						
<u>Vacuum Pressure-5 Cycles Test</u>	6	3	1	2	5	4
Treatment Mean **	9	18	18	20	20	36
<hr/>						

* Means underscored by the same line are not significantly different at the 5% level of significance.

** Means above refer to treatments as follows:

1. UFi-C-6
2. UFi-C-10
3. UFi-F30-6
4. UFi-F30-10
5. UFi-B30-6
6. UFi-B30-10

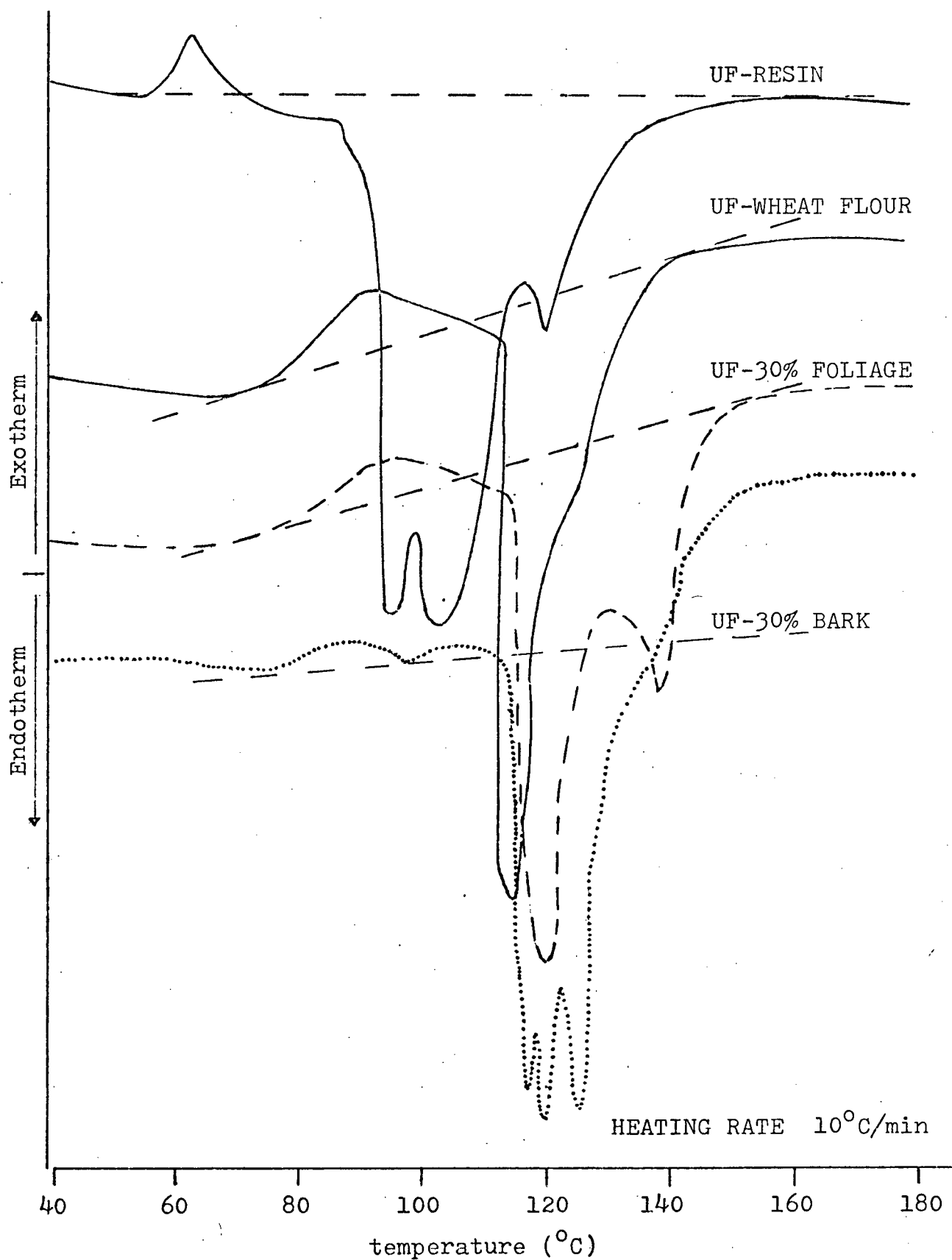


Figure 1. DSC thermograms of UF resin with wheat flour, 30% foliage and 30% bark.

6 min pressing time
10 min pressing time

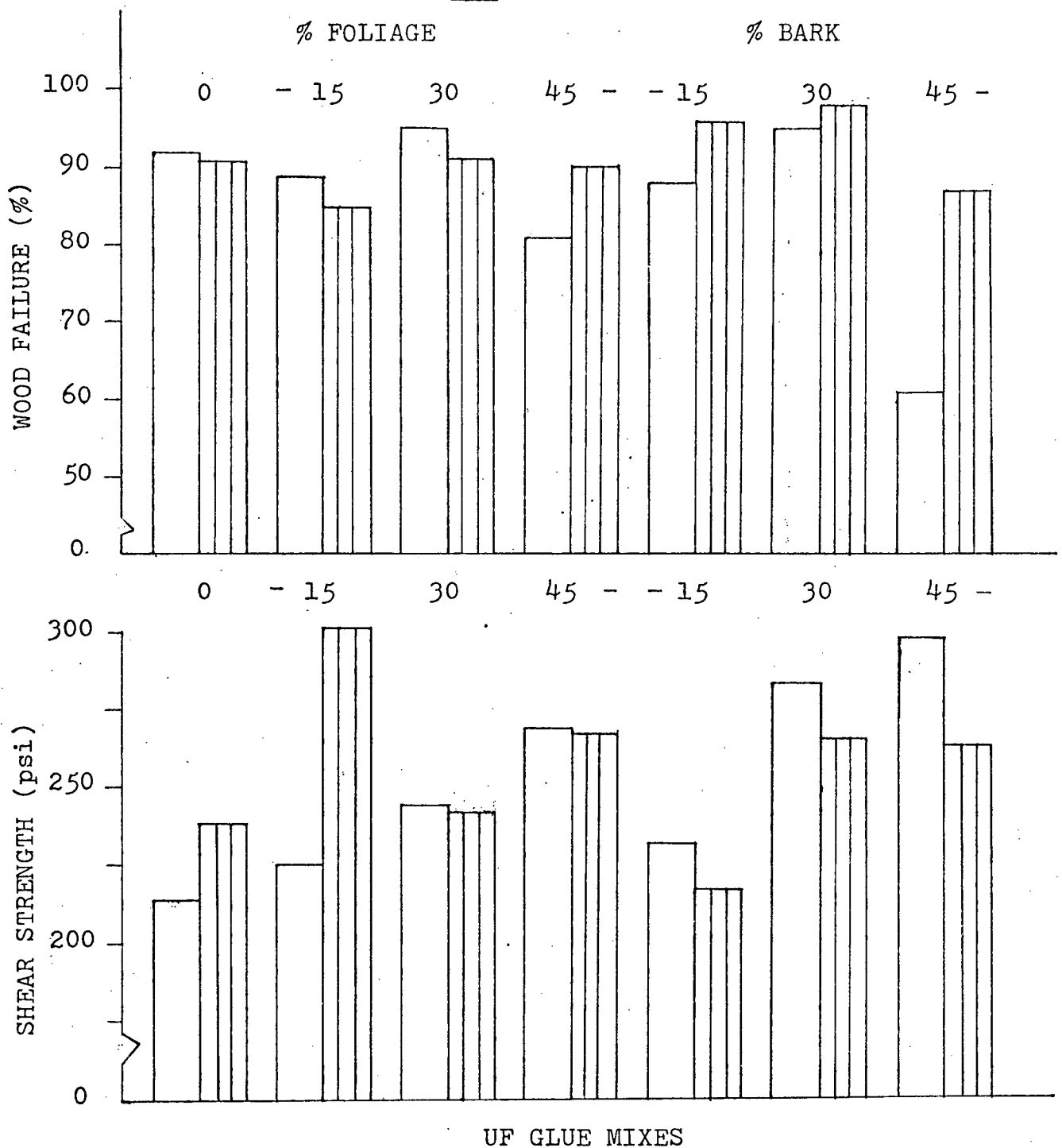


Figure 2. Dry-shear strengths and wood failure percentages for treatments bonded with the commercial UF glue.



6 min pressing time



10 min pressing time

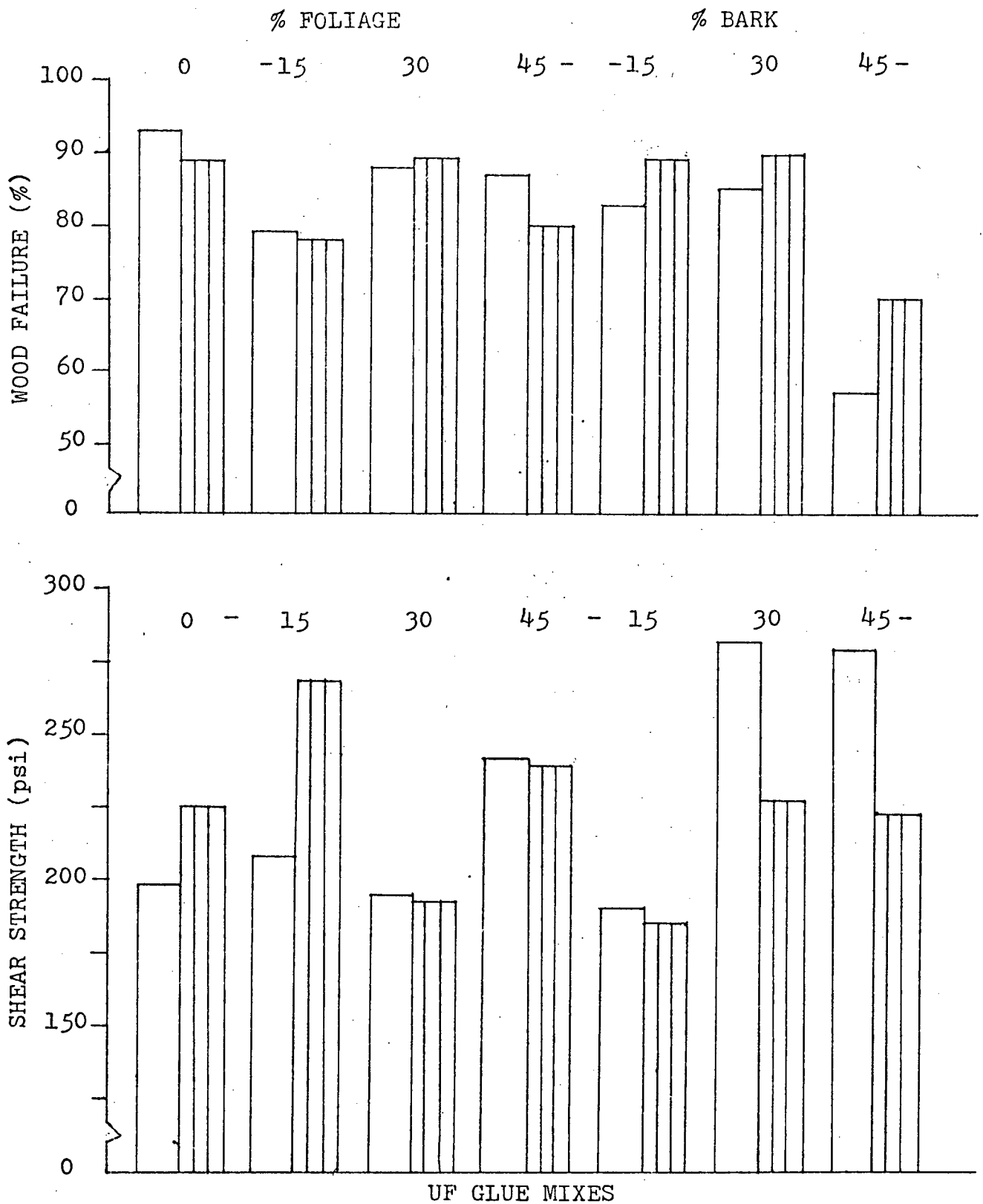


Figure 3. Vacuum pressure-shear strengths and wood failure percentages for treatments bonded with the commercial UF glue.

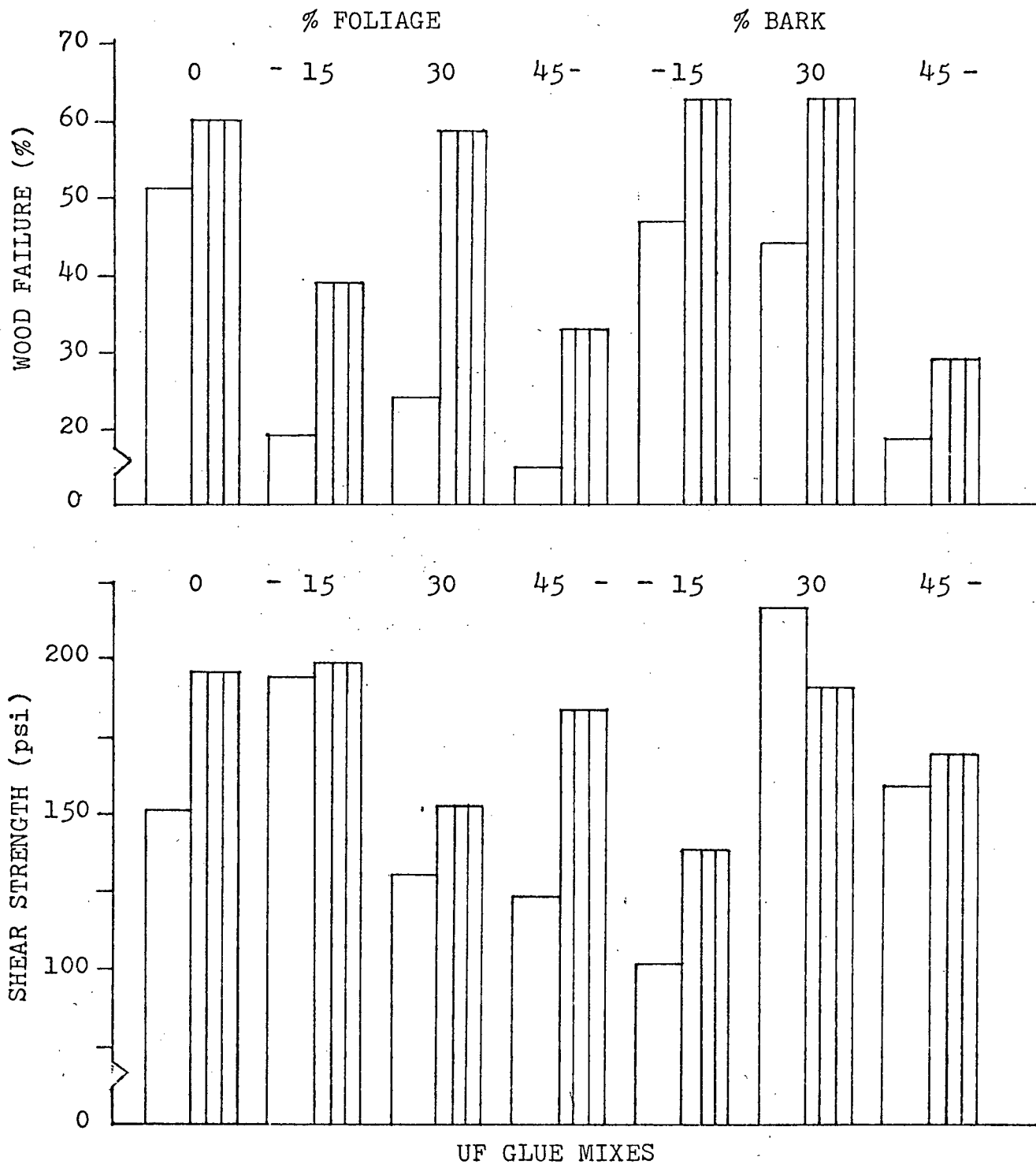
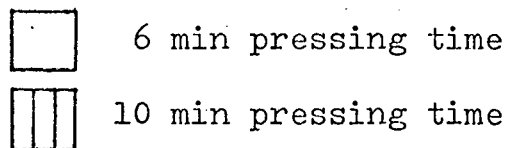


Figure 4. Vacuum pressure-five cycle shear strengths and wood failure percentages for treatments bonded with the commercial UF glue.

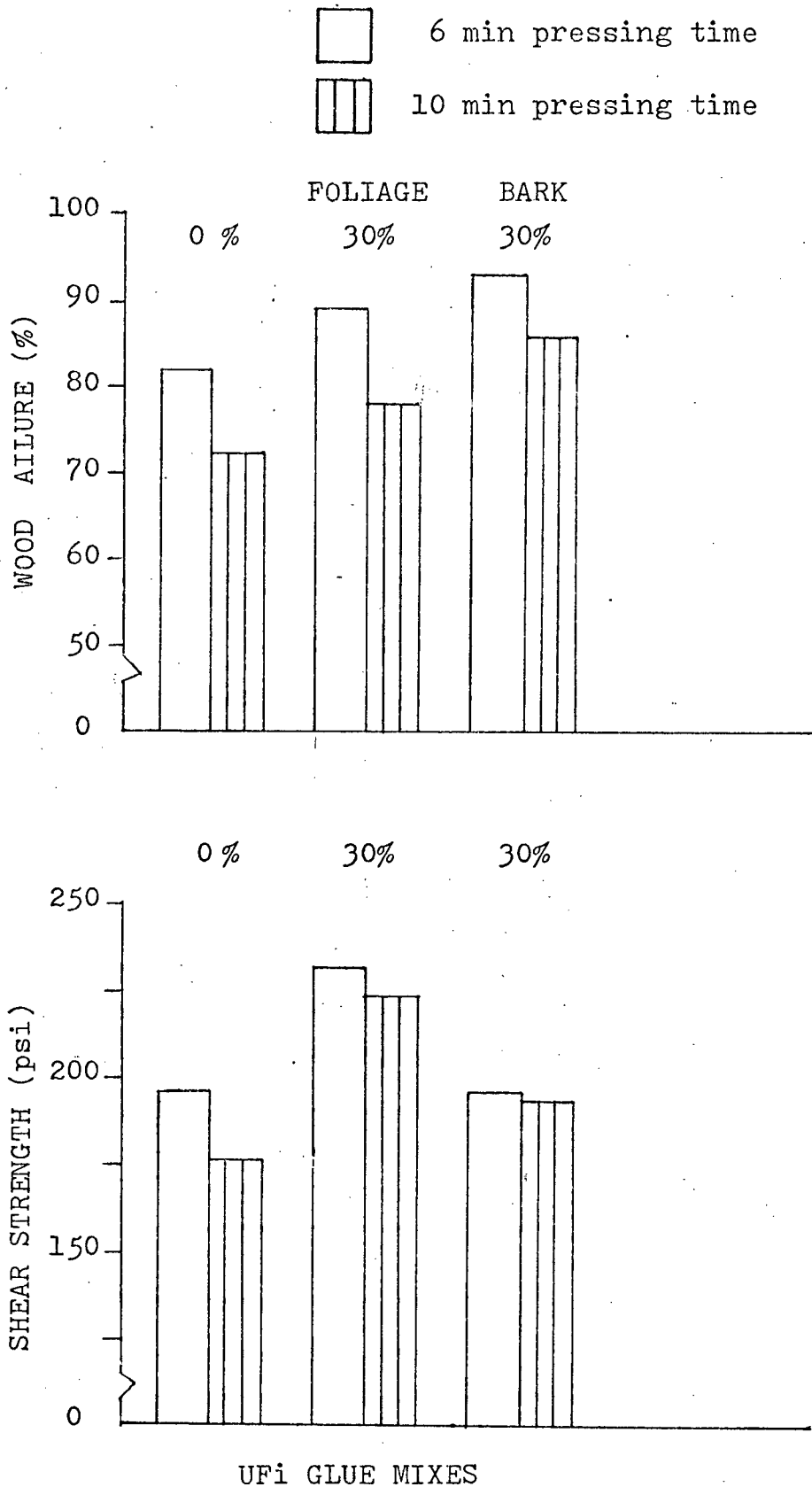


Figure 5. Dry shear strengths and wood failure percentages for treatments bonded with the laboratory UF glue (UFI).

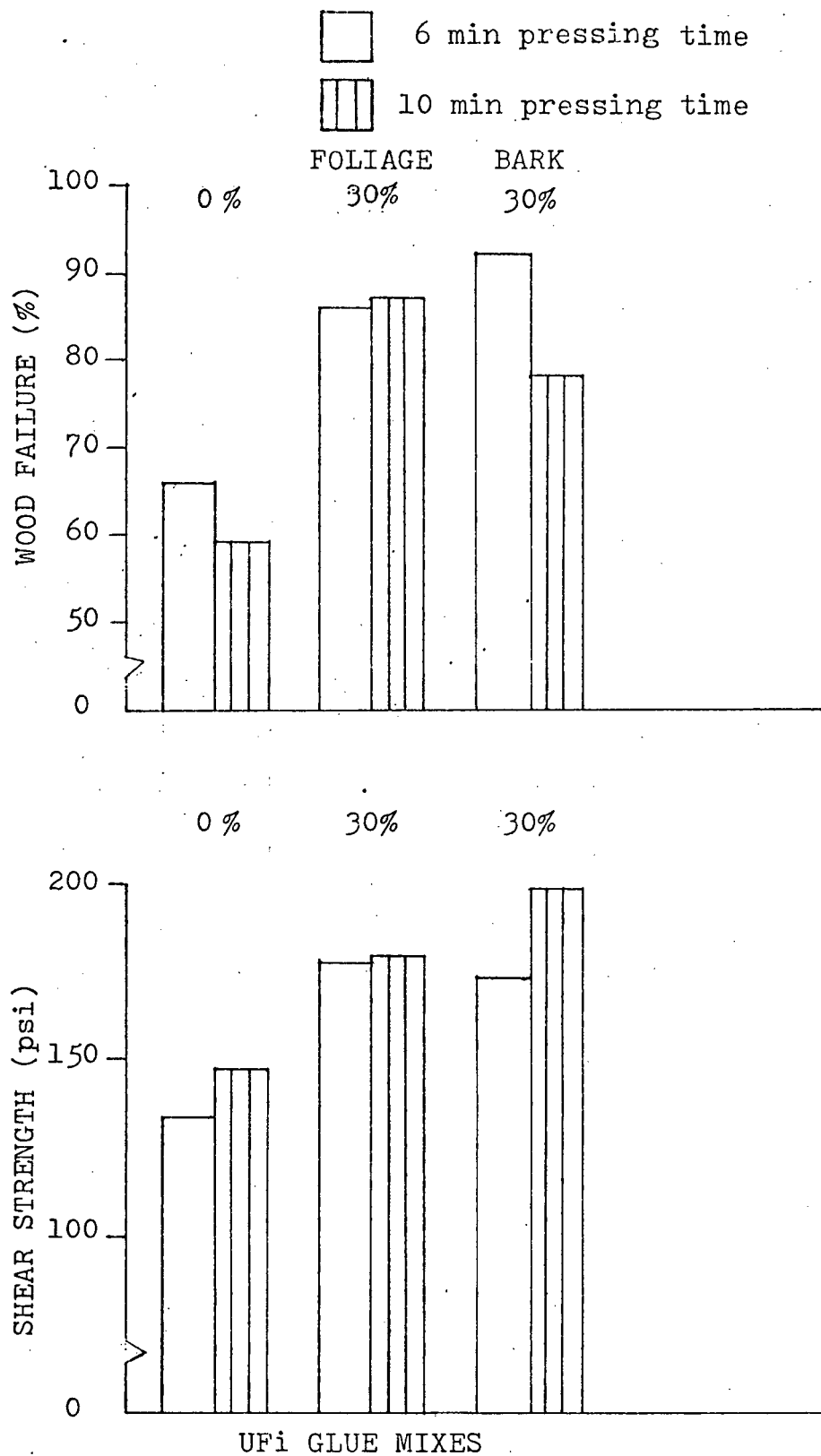


Figure 6. Vacuum pressure-shear strengths and wood failure percentages for treatments bonded with the laboratory UF glue (UFi).

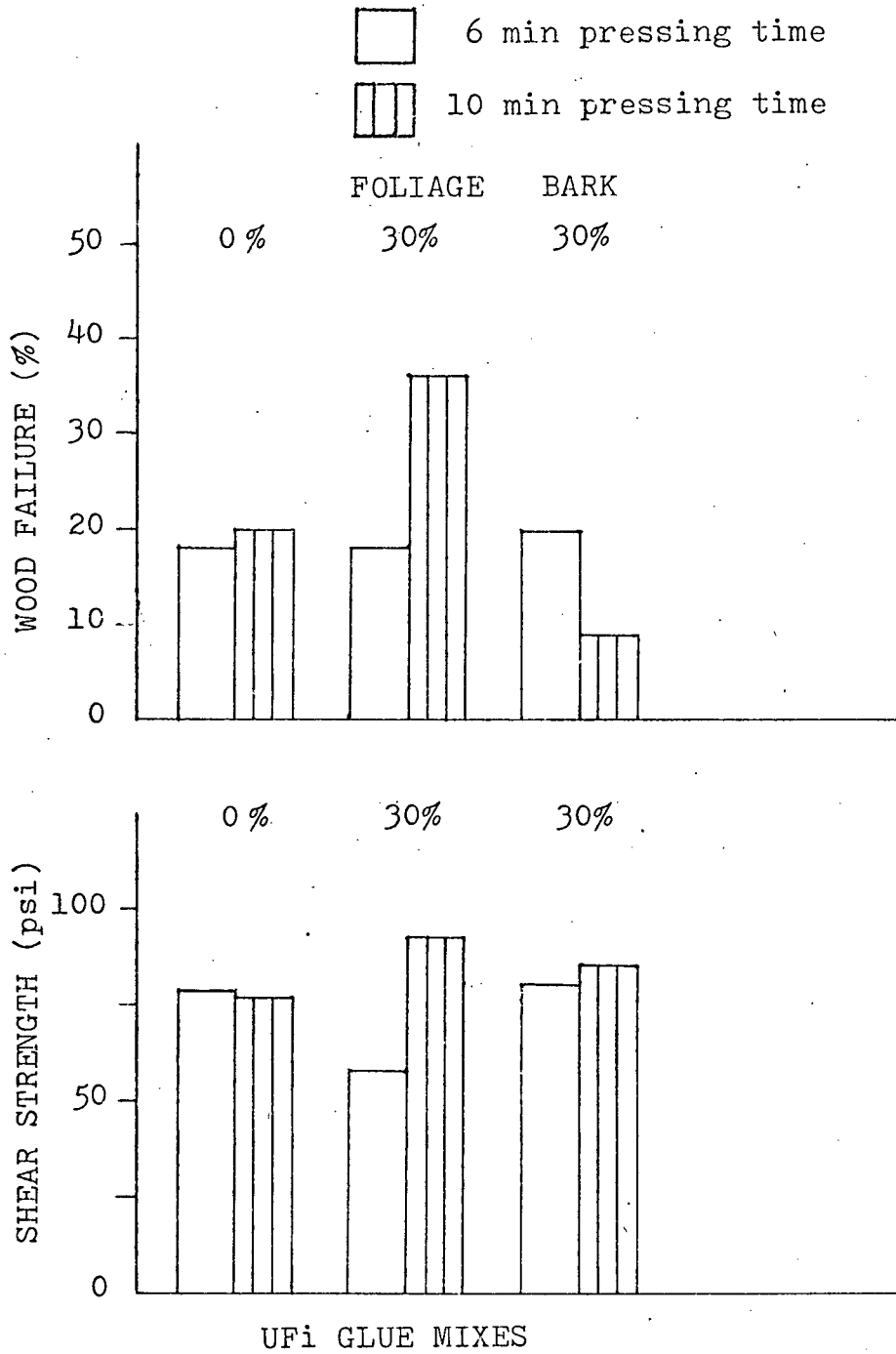


Figure 7. Vacuum pressure five cycle-shear strengths and wood failure percentages for treatments bonded with the laboratory UF glue (UFi).

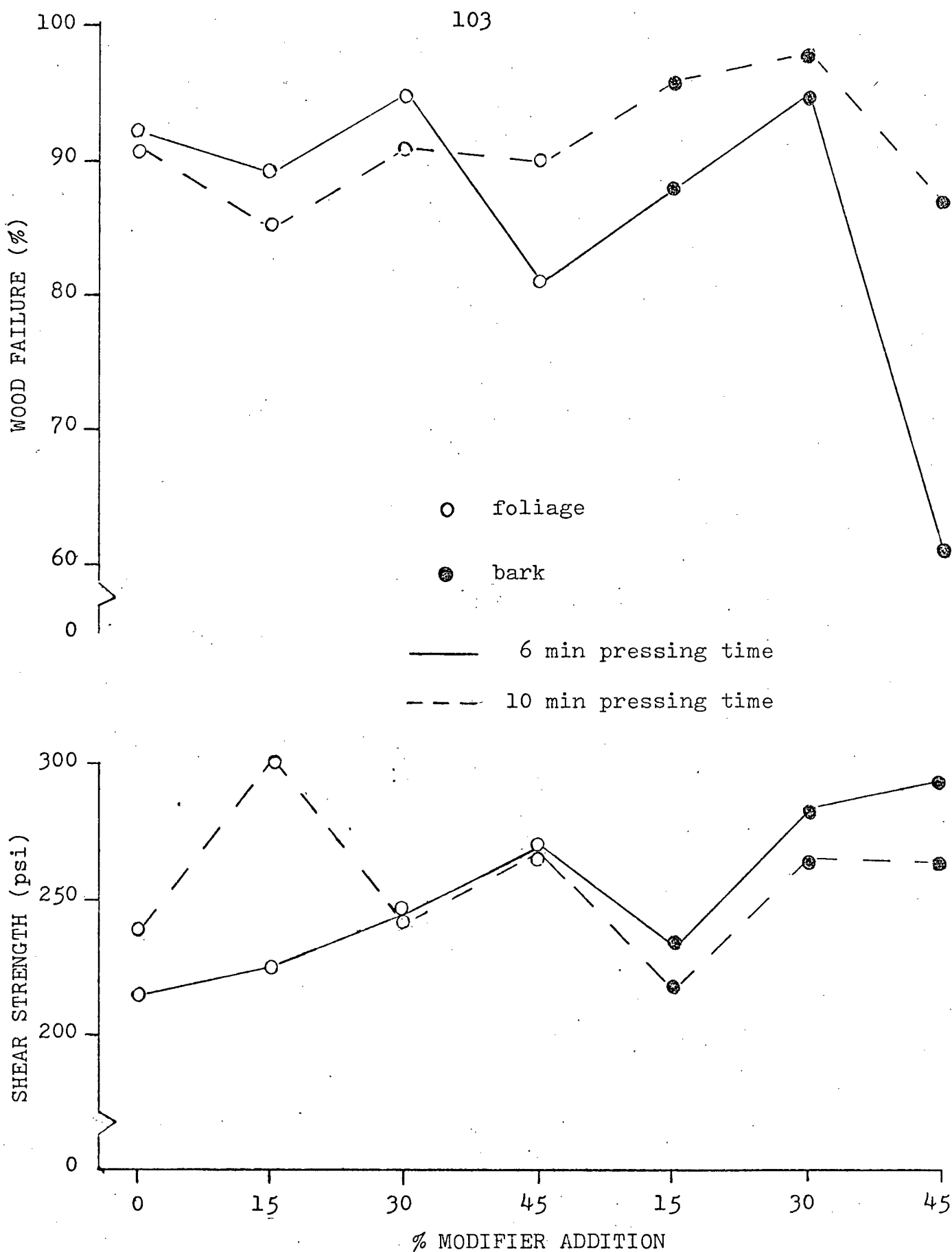


Figure 8. Dependence of plywood bond quality on the UF glue mix and pressing time interaction according to dry-shear strengths and wood failure percentages.

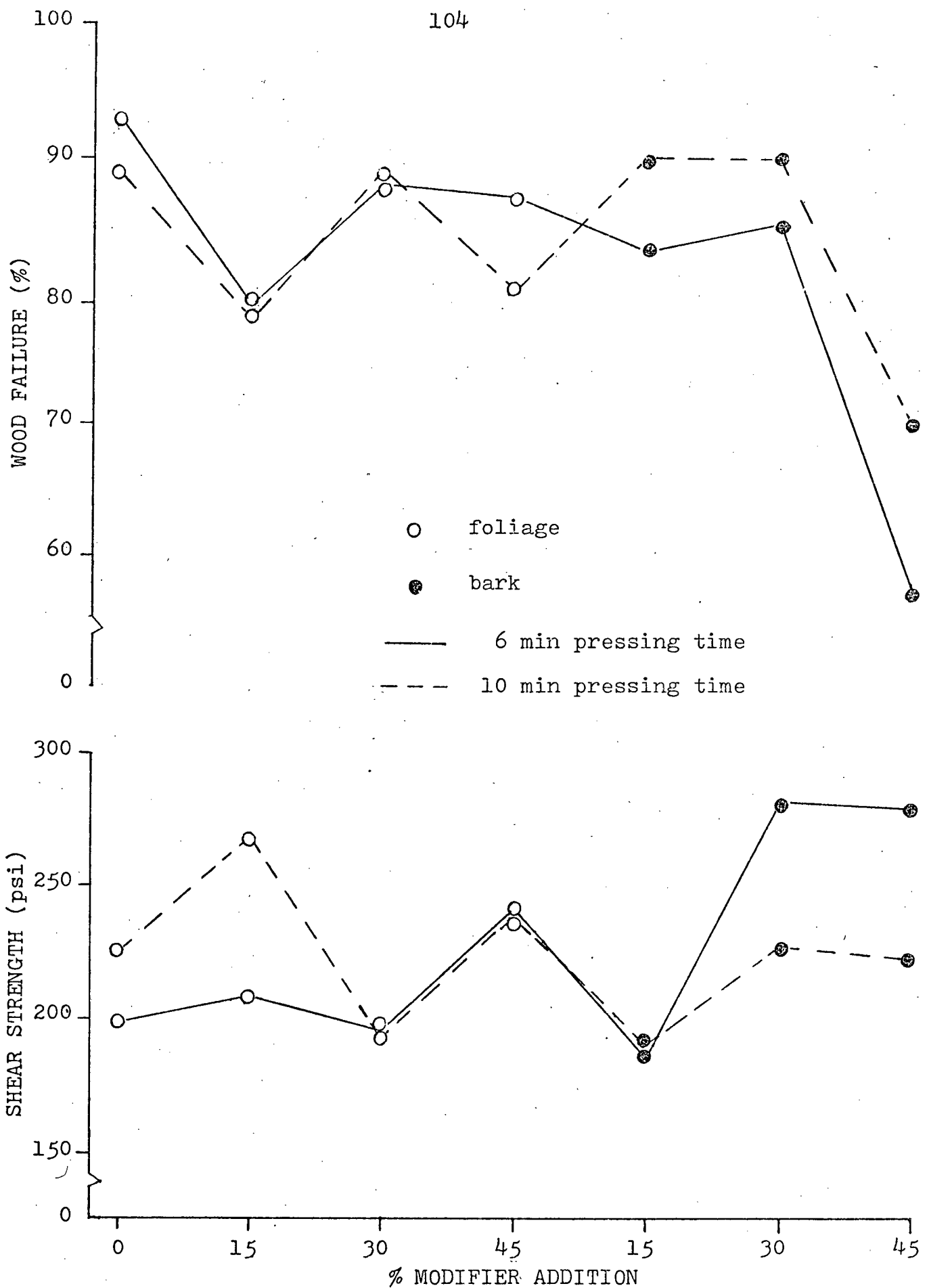


Figure 9. Dependence of plywood bond quality on the UF glue mix and pressing time interaction according to vacuum pressure-shear strengths and wood failure percentages.

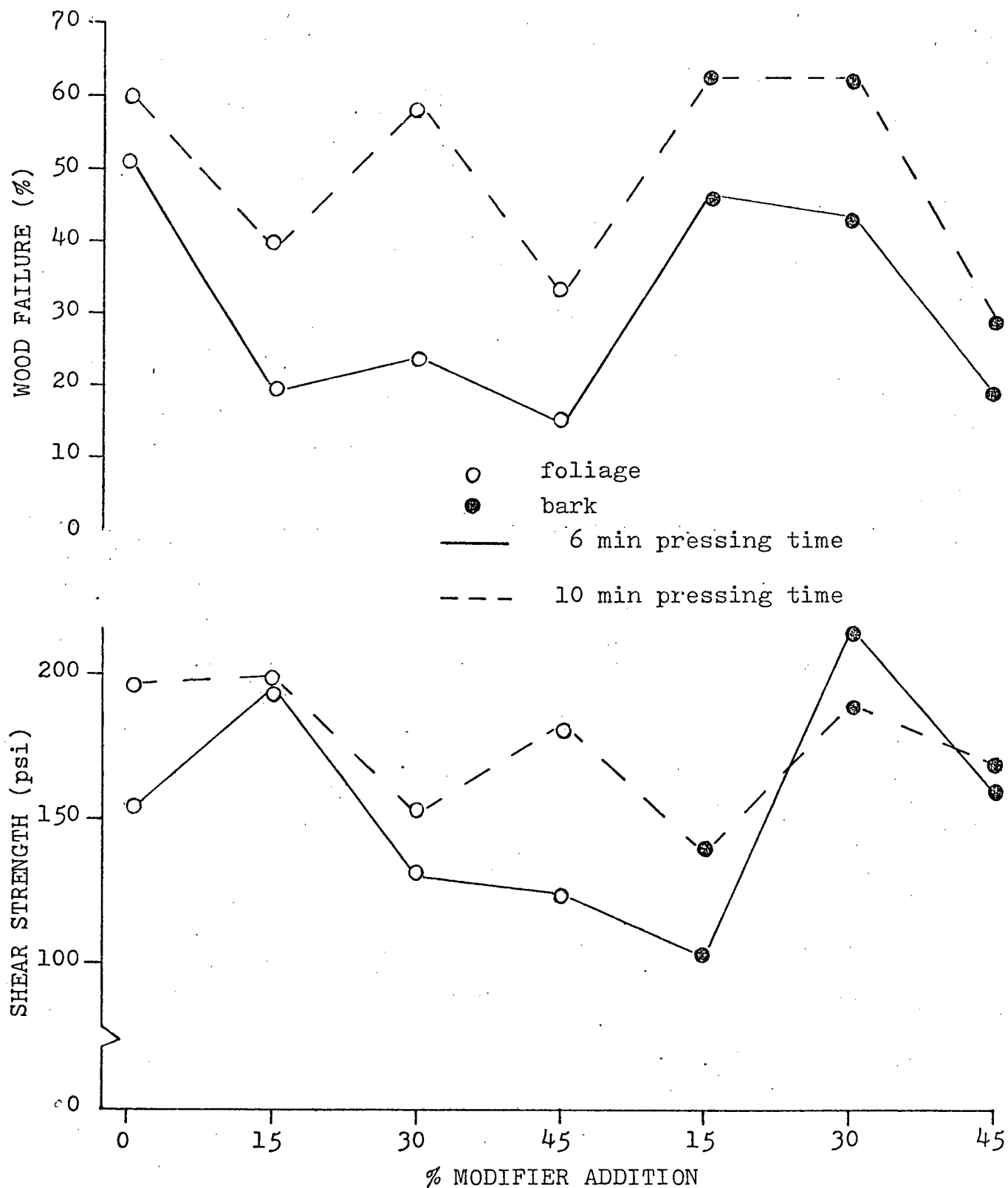


Figure 10. Dependence of plywood bond quality on the UF glue mix and pressing time interaction according to vacuum pressure five cycles-shear strengths and wood failure percentages.

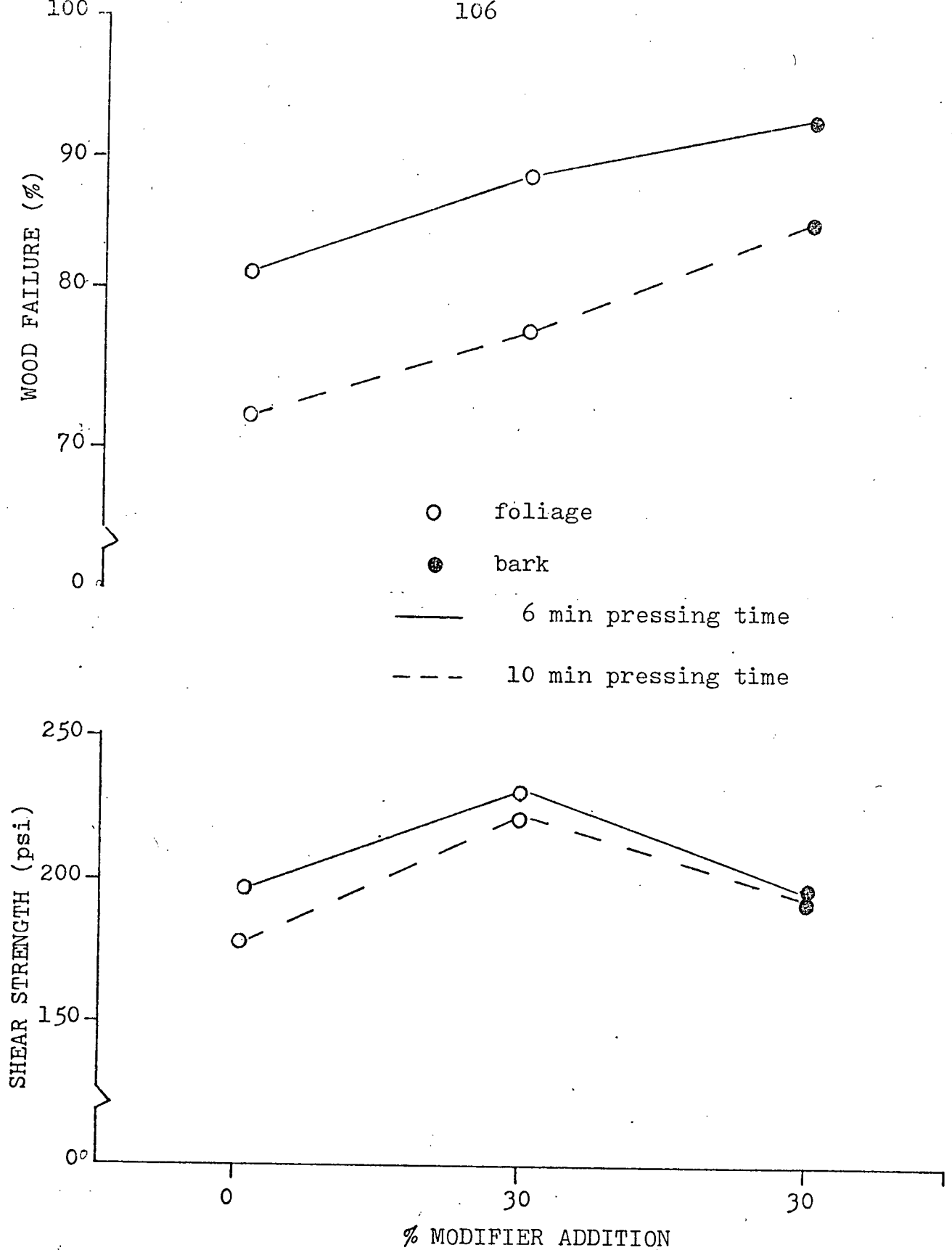


Figure 11. Dependence of plywood bond quality on the UFi glue mix and pressing time interaction according to dry-shear strengths and wood failure percentages.

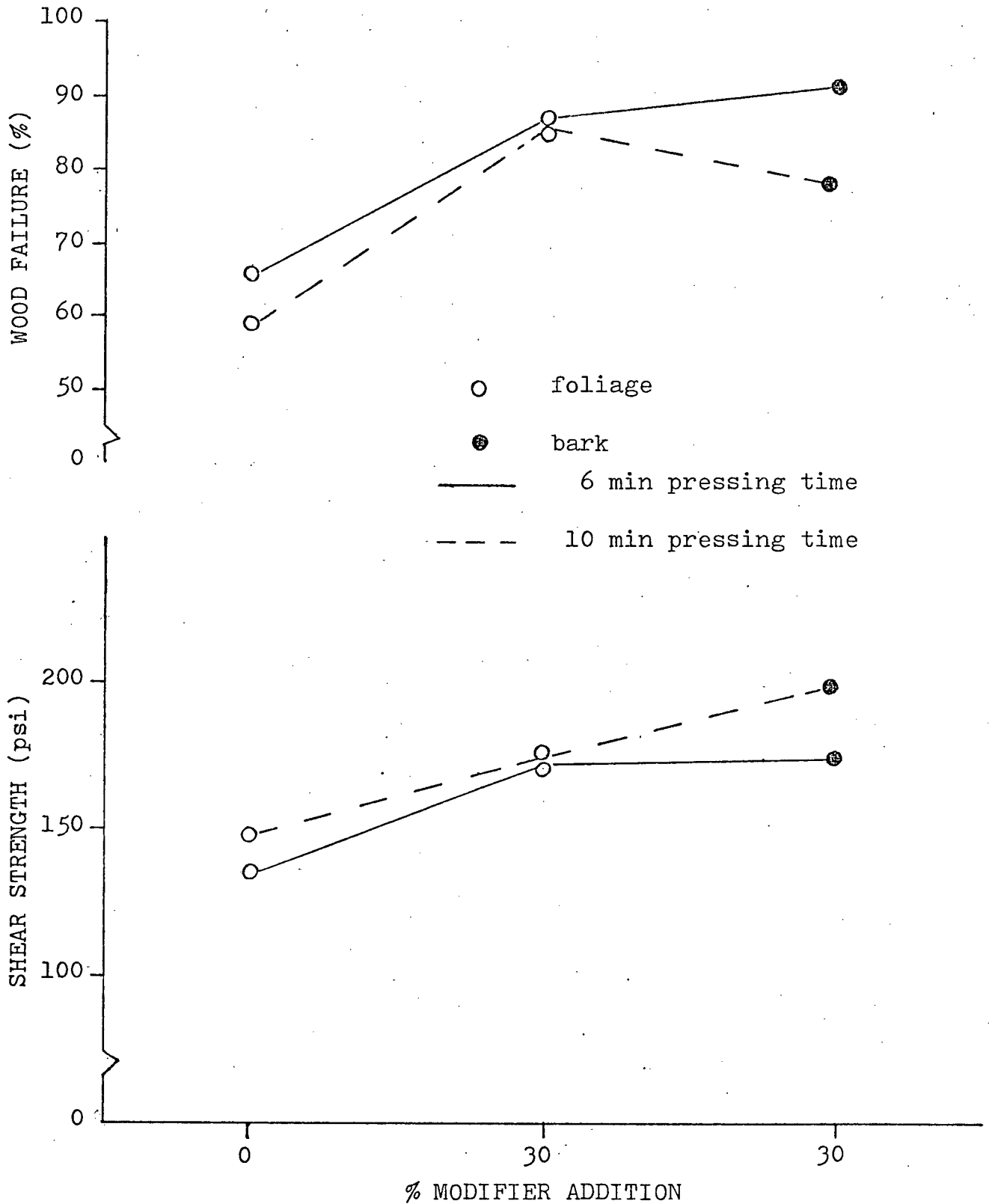


Figure 12. Dependence of plywood bond quality on the UFi glue mix and pressing time interaction according to vacuum pressure one cycle-shear strengths and wood failure percentages.

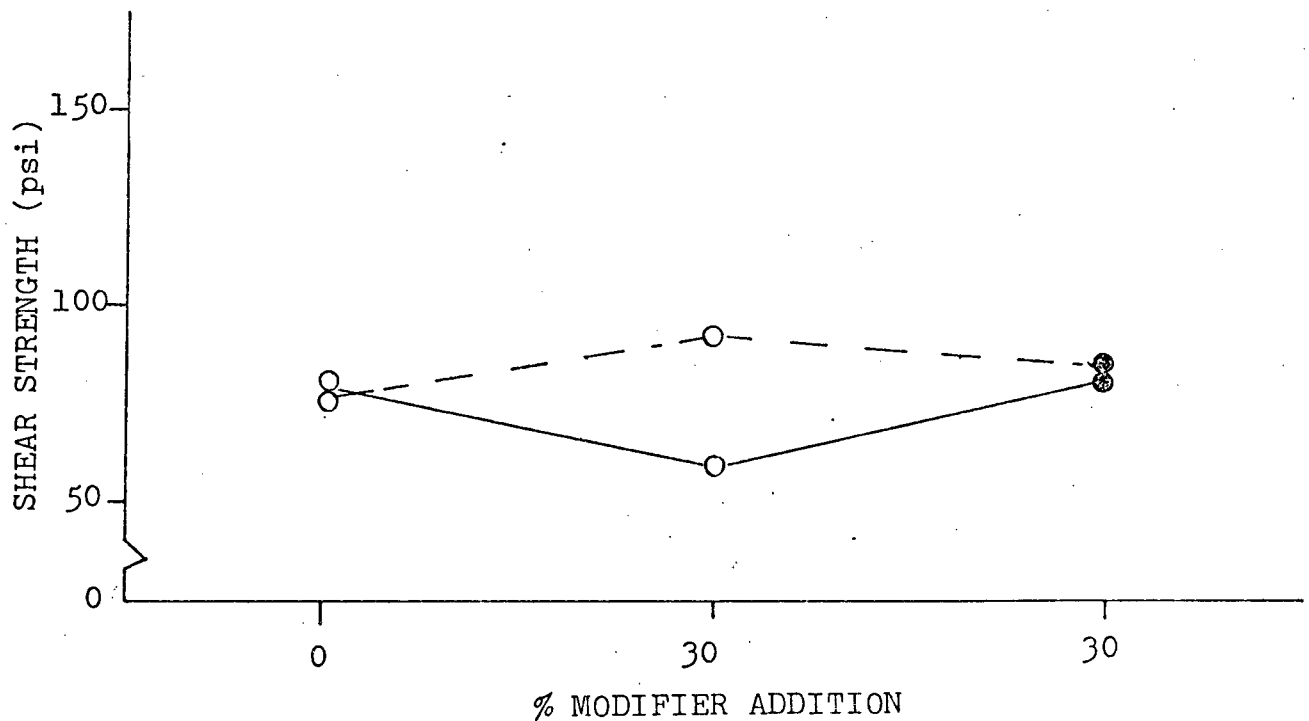
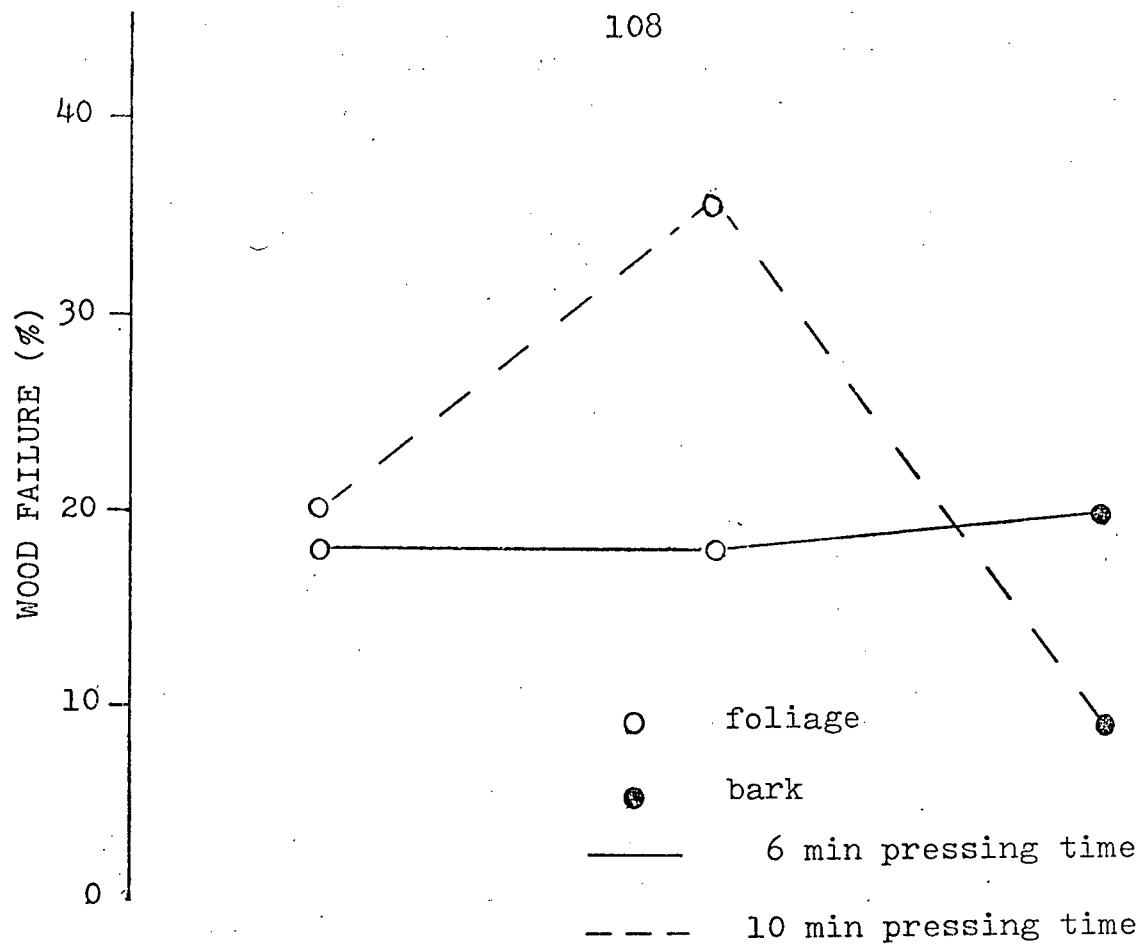


Figure 13. Dependence of plywood bond quality on the UFi glue mix and pressing time interaction according to vacuum pressure five cycles-shear strengths and wood failure percentages.

APPENDIX I. Specification and mixing directions
for the standard Casco UF 109 glue.



ADHESIVES
AND RESINS

CASCO UF 109

PRODUCT TYPE: UF109 is a high solids, aqueous, urea-formaldehyde resin solution.

APPEARANCE: A clear to slightly cloudy, viscous liquid when fresh, becoming increasingly cloudy on storage.

PROPERTIES:

	<u>Specifications</u>	<u>Test Method</u>
Viscosity at 70°F. MM 26D	44 ± 5	F-302
Viscosity at 77°F. Centipoises	525 ± 75	F-302.4
% Solids Content	63.0 ± 2.0%	F-303.1(WCAM)
pH (Beckman Model H2)	8.4 ± 0.2	F-304
Specific gravity 60°/60°F	1.302 ± 0.003	F-301
% Free Formaldehyde	2.0 ± 0.5	F-305.1
Gel Time at 110°F.		
With 5 cc 10% "Y" catalyst per 100 gms. UF109		15 ± 2 mins.
With 10 gms 109AR hardener per 100 gms UF109		23 ± 3 mins.
With 10 gms 221 hardener per 100 gms UF109		42 ± 4 mins.

APPLICATION: The manufacture of plywood; veneering, lumber laminating, edge gluing, and general assembly gluing when formulated with the appropriate catalysts and/or extenders and fillers.

STORAGE & HANDLING: The storage life of UF109 is approximately 6 months at 70°F. Low temperatures will increase the storage life and, conversely, higher temperatures will decrease the storage life appreciably. UF109 is classified as a liquid resin, essentially non-volatile and non-flammable. The free formaldehyde present in UF109 can cause dermatitis and it is recommended that gloves and goggles be used when handling this resin.

Contamination with iron will tend to darken most urea-formaldehyde resins and to avoid this occurring in UF109 it is recommended that the resin be stored in heresite, polyethylene, or equivalent lined drums or tanks.

These recommendations and suggestions for the use of our materials are based on our best experience and knowledge but we do not guarantee the results to be obtained in customer's processes. Prices subject to change without notice.

BORDEN CHEMICAL WESTERN

DIVISION OF THE BORDEN COMPANY, LIMITED

Standard Plywood UF Glue Mix

Mixing Directions

Water	- 851 g
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Sterox	- 3.3 g
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Start mixing

Wheat flour	- 700 g
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Mix 2-4 minutes

Resin (63% UF 109)	- 1500 g (945 g resin solids)**
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Mix until smooth

Ammonium chloride	- 12 g
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Aqua ammonia	- 12 g
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3078 g

Resin solids as % total mix	- 30.7
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Total solids as % total mix	- 53.8
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Spread, MDGL, approx.	- 70 lb/MDGL* (32 kg/100 m ²)
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* MDGL: 1000 square foot of double glue line

** 15, 30 and 45% foliage and bark additions were based on resin solids weight.

APPENDIX II. Code for treatments identification

Code for Treatments Identification

Treatment	Glue	Modifier addition (%)	Pressing time (min)	Code
<u>First stage</u>				
1	UF	0	6	UF-C-6(Control)
2		0	10	UF-C-10(Control)
3		Foliage 15%	6	UF-F15-6
4		Foliage 15%	10	UF-F15-10
5		Foliage 30%	6	UF-F30-6
6		Foliage 30%	10	UF-F30-10
7		Foliage 45%	6	UF-F45-6
8		Foliage 45%	10	UF-F45-10
9		Bark 15%	6	UF-B15-6
10		Bark 15%	10	UF-B15-10
11		Bark 30%	6	UF-B30-6
12		Bark 30%	10	UF-B30-10
13		Bark 45%	6	UF-B45-6
14		Bark 45%	10	UF-B45-10
<u>Second Stage</u>				
1	UFi*	0	6	UFi-C-6(Control)
2		0	10	UFi-C-10(Control)
3		Foliage 30%	6	UFi-F30-6
4		Foliage 30%	10	UFi-F30-10
5		Bark 30%	6	UFi-B30-6
6		Bark 30%	10	UFi-B30-10

* UFi, laboratory formulated low molecular weight UF resin.

Example:

UF-F15-6 — pressing time
 — addition level
 — UF resin type